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TRANSACTIONS.

CONTENTS

I.—*Investigations on the Dependence of Rotatory Power on Chemical Constitution. Part XIII.* The Spatial Configuration of the Unbranched Aliphatic Chain.*

By Robert Howson Pickard, Joseph Kenyon, and Harold Hunter.

Adopting the accepted view that the carbon atom may be considered as a sphere with its four valencies directed mainly to the vertices of an inscribed tetrahedron, Frankland (T., 1899, **75**, 368) suggested that a chain of such atoms might be expected to form a spiral which would complete one turn at about the fifth member, and that we should accordingly look for anomalies in physical properties at that point. Attention must be directed to the fact, however, that the spiral is by no means the only form which the chain can assume, nor, considered solely on mathematical grounds, is it the most probable. For, after the third member, there are three possible directions in space for extension of the chain to take place, only one of which will lead to the spiral configuration. This is the case at each additional member after the third, and therefore the probability of a chain of such atoms assuming a spiral form as a result of pure chance is at most $1/3^{(n-3)}$, where n is the number of atoms in the chain. That is to say, for a four-membered chain the odds are at least 2 to 1 against, for a

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* In this paper references are made to Part I, T., 1911, **99**, 45; Part II, T., 1912, **101**, 620; Part III, *ibid.*, 1427; Part V, T., 1914, **105**, 830; Part VII, *ibid.*, 2226; Part VIII, *ibid.*, 2262; Part IX, *ibid.*, 2644; Part XII, T., 1915, **107**, 115.

five-membered chain they are 8 to 1 against, and for a thirteen-membered chain they are 60,000 to 1 against such a form being assumed as a result of pure chance.

A review of our previous work bearing on this point shows that Frankland's conception of the spiral chain may now be extended to include some heterocatenic substances in which one atom of oxygen is included in the chain.

It has been shown in the earlier parts of these investigations that the optical rotatory powers of members of many homologous series vary in a regular manner with molecular weight. In view of what has been said above, then, it is a fact of great significance that this regularity is often disturbed at perfectly definite points in the series, after which the normal variation is resumed until the next point is reached, and so on. These points occur when an unbranched chain of carbon (or carbon and oxygen) atoms contains five (or a multiple of five) members. Occasionally this effect is noticed at the points where the chain contains six or eleven atoms, but in this connexion it must be remembered that the valency directions of the carbon atom are not invariably inclined at an angle of 109° 28′ to each other as the conception of rigid bonds by van't Hoff and by Baeyer would lead us to expect. Rather is it the case, as Ingold and his colleagues (T., 1921, **119**, 305, *et seq.*) have recently shown, that the angle between the valency directions of the carbon atom depends on the volumes of the atoms. or groups to which it is attached. Thus the normal angle between the carbon-to-carbon valencies in a polymethylene chain is not, 109·5°, but 115·3°, and therefore there will be more atoms in one complete turn of the spiral in the case of an unsubstituted polymethylene chain than in the case of a substituted chain. Then, again, in the case of the oxygen atom, we are not certain of the directions in which its valencies mainly act. Its volume is almost identical with that of the carbon atom; it frequently—much more frequently than was formerly supposed—exercises quadri-valency and may therefore perhaps be regarded as nearly identical with the carbon atom so far as its influence on the configuration of a chain is concerned. But it would require only a slight change of the " intervalent " angle to modify the shape of the chain sufficiently to cause irregularities to appear at the sixth or eleventh instead of the fifth and tenth members of a series, and either of the above causes would be amply sufficient to determine such a change.

Up to the present, marked irregularities in the numerical value of a physical property in a homologous series at points where a spiral chain may be assumed to have completed an integral number of turns have been detected only in rotatory power. Similar

irregularities, although much less in amount, have, however, been observed in the densities of members of homologous series, for example, in the *iso*propyl-*n*-alkylcarbinols (Part II, p. 637), the esters of *ac*-tetrahydro-β-naphthol (Part III, p. 1430), the ethyl-*n*-alkylcarbinols (Part IV, p. 1935), and the esters of *iso*pulegol (T., 1920, **117**, 1248). In the last case this irregularity is reflected in the values of the molecular refractive power ($[R_L]_\lambda^k$). These other irregularities are, however, very small in amount, being often very little greater than the experimental error, and it would be rash to base conclusions on consideration of these alone. But as confirmatory evidence they are helpful, although we are forced to the conclusion that it is the highly constitutive nature of optical activity which renders it so pre-eminently useful in the elucidation of the finer details of molecular architecture.

Some of the cases of abnormality of rotatory power associated with the presence within the molecule of a chain containing five, ten, or fifteen atoms of carbon or of carbon and oxygen may now be discussed.

In the homologous series of methyl-*n*-alkylcarbinols (Part I, p. 49), the rotatory power at 20° in the homogeneous state of the propyl member is abnormally high compared with those of the rest of the series. This abnormality is intensified at 90°. When the rotatory powers are determined in solution in benzene and in ethyl alcohol (Part VI, p. 1928), in addition to the abnormality at the propyl member, we find similar ones at the amyl, octyl, and decyl members.

Representing the series by the general formula

$$C_nH_{2n+1}\cdot CH(OH)\cdot CH_3$$
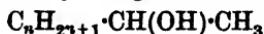
we see that when $n = 5$ or a multiple thereof, the growing chain attached to the asymmetric carbon atom will have completed one or more turns of the spiral. When, on the other hand, n is two less than 5 or a multiple thereof, the whole chain of carbon atoms in the molecule will have made one or more complete turns of the spiral.

The temperature–rotation curves for the ethyl and *n*-propyl members of the alkyl*iso*propylcarbinols (Part II, p. 623) are similar to each other and differ from those of the rest of the series. Writing down the formulæ of these alcohols

$$\overset{1}{C}H_3\cdot\overset{2}{C}H_2\cdot\overset{3}{C}H\cdot\overset{4}{C}H\cdot\overset{5}{C}H_3 \qquad \text{ethyl}iso\text{propylcarbinol}$$
$$OH\ \ CH_3$$

$$\overset{1}{C}H_3\cdot\overset{2}{C}H_2\cdot\overset{3}{C}H_2\cdot\overset{4}{C}H\cdot\overset{5}{O}H \qquad n\text{-propyl}iso\text{propylcarbinol,}$$
$$CH(CH_3)_2$$
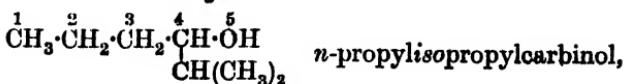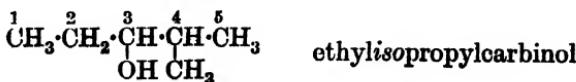
it is immediately obvious that in the former case we have a chain of five carbon atoms, and in the latter, one of four carbon and one oxygen atom.

Again, ethyl-n-propylcarbinol (Part VI, p. 1924),

$$\overset{1}{C}H_3 \cdot \overset{2}{C}H_2 \cdot \overset{3}{C}H_2 \cdot \overset{4}{C}H \cdot \overset{5}{O}H$$
$$CH_2 \cdot CH_3$$
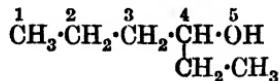
has a low rotation compared with the other ethylalkylcarbinols— it may be that this is due to the chain of one oxygen and four carbon atoms in the molecule.

Perhaps the most striking example of these irregularities is to be found in the series of ethylalkylcarbinols (Part IV). If the specific rotatory powers of these alcohols be plotted as ordinates with the number of carbon atoms in the growing alkyl chain as abscissæ, it is found that the n-amyl and n-hexyl and again the n-decyl, n-undecyl, and n-dodecyl members have rotatory powers considerably in excess of what may be regarded as the normal value deduced from considerations of the rotatory powers of the other members of the series. Here again we see the influence of a chain of five and six and also ten and eleven carbon atoms, and in this particular case the rotations are measured in the homogeneous state, so that we do not have to consider the effect of solution, which is at present very little understood.

The effect of solvent and also of change of temperature on these irregularities is exemplified in the series of esters of l-isopulegol (T., 1920, **117**, 1248). Measured in the homogeneous state at 20°, the specific rotatory powers of these esters show a regular decrease, after the first three members, in their numerical value. This regularity is sharply interrupted at the n-valerate and again at the n-decoate and n-undecoate. At 80°, however, the irregularity at the n-valerate is much less in amount and the irregularity at the n-decoate and the n-undecoate has disappeared entirely.

In ethyl alcoholic solution, there are, in addition, indications of similar irregularities at the propionate and n-octoate. The explanation of these results becomes clear when we consider the structural formulæ for these esters (I).
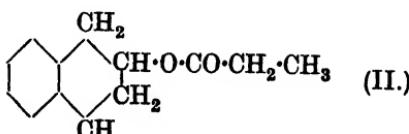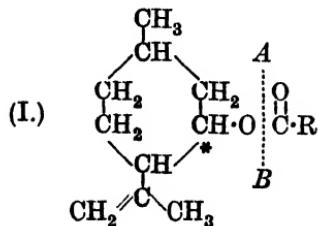
It is obvious that when R contains four or nine (ten) carbon atoms, that is, in the cases of the *n*-valerate and *n*-decoate (undecoate) the " ester " chain to the right of AB will contain five and ten (eleven) carbon atoms and may be assumed to have completed just one or two turns of the spiral, respectively.

When R contains two or seven atoms, on the other hand, that is, at the propionate or *n*-octoate, the whole chain up to the asymmetric carbon atom * will contain either four carbon atoms and one oxygen atom or nine carbon atoms and one oxygen atom and may again be imagined to have completed whole turns of the spiral as before.

It seems evident, too, that some similar cause promotes the maximum molecular rotatory power exhibited among the esters of tetrahydronaphthol (Part III, p. 1430) by the propionate (II), and also the irregular values of the rotatory powers of the esters of 1-naphthyl-*n*-hexylcarbinol (Part IX, p. 2648), particularly of the propionate and octoate in which the acyl chains vary by five carbon atoms, whilst the abnormal values (under some conditions of solution) of the acetate, $\overset{1}{C}H_3 \cdot \overset{2}{C}O \cdot \overset{3}{O} \cdot \overset{4}{C}H(C_{10}H_7) \cdot \overset{10}{C}_6H_{13}$, and of the heptoate are also noteworthy.

Again, the relatively high rotation of β-pentyl *n*-valerate, $\overset{4}{C}_4H_9 \cdot \overset{5}{C}O \cdot \overset{6}{O} \cdot \overset{7}{C}HMe \cdot \overset{10}{C}_3H_7$, (Part V, p. 831), may be due to the ten-atomed chain—five of carbon, one of oxygen, and four other carbon atoms.

Further, among the acetates of the carbinols $C_2H_5 \cdot CH(OH) \cdot C_nH_{2n+1}$ described in Part VII (p. 2231) the numerically high positive rotation of *d*-β-butyl acetate, $CH_3 \cdot CO \cdot O \cdot CHEt \cdot CH_3$, and the abnormally high negative rotation (in carbon disulphide) of the acetate of *d*-γ-nonanol, $CH_3 \cdot CO \cdot O \cdot CHEt \cdot C_6H_{13}$, are peculiarities which may be due to the presence in these compounds of un-branched chains of carbon and oxygen atoms numbering in all five and ten, respectively. Similar deviations from what may be called the normal rotatory power have been observed (Part VII, p. 2229) in the cases of γ-nonyl hexoate, $C_5H_{11} \cdot CO \cdot O \cdot CH(C_6H_{13}) \cdot C_2H_5$, and the undecoate, $C_{10}H_{21} \cdot CO \cdot O \cdot CH(C_6H_{13}) \cdot C_2H_5$, compounds which may be regarded as containing ten and fifteen atoms (one of these being oxygen), respectively, in an unbranched chain.

Other examples of this kind can be cited from the literature, and it was felt that the examination of the formic esters of the simple optically active secondary alcohols would furnish a test case of some theoretical value. When specific rotatory power is plotted against molecular weight for various series of esters, it is observed that in the case of, for example, the β-octyl esters (Part V), the γ-nonyl esters (Part VII), and the esters of benzylmethylcarbinol

(Part VIII) either the acetate or the propionate occupies an anomalous position in that it does not fit on the curve illustrating the connexion between molecular weight and rotatory power. In the case of the esters of β-butanol (Part V), on the other hand, both

FIG. 1.

Number of carbon atoms in growing acyl chain.
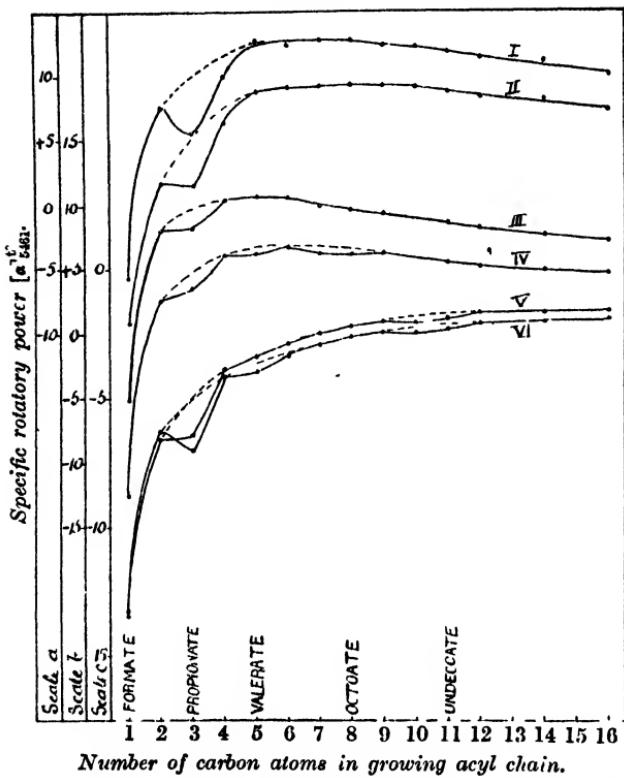
The specific rotatory powers [a]²⁰₅₄₆₁, in the homogeneous state of the normal esters of

d-Benzylmethylcarbinol at   20°   (I)⎫
                             and at 120°   (II)⎭ *Scale a*
d-β-Octanol   at   20° (III)⎫
                             and at 120° (IV)⎭ *Scale b*
and of d-γ-Nonanol   at   20° (VI)⎫
                             and at 120°   (V)⎭ *Scale c*

The broken curve in each case represents the apparent normal rate of increase of specific rotatory power with molecular weight.

the acetate and the propionate fall into line with the other members of the series.

It was therefore decided to make these four series of esters more complete by the inclusion of the formates. The results of the polarimetric measurements are illustrated in the figure, where they

are co-ordinated with the results obtained for the other esters of the series. They show that in each case it is the propionic member of the series rather than the acetate which shows irregularity of rotatory power, although the results of further work with optically active ethers (Parts XIV and XV, this vol., pp. 14 and 22) seem perhaps more in accordance with the idea that the acetate is the irregular member. Curve IV is particularly interesting as showing the effect of a rise in temperature in bringing to light the irregularity, latent at lower temperatures, in the rotatory power of the n-valerate and of the n-octoate of d-β-octanol.

It may therefore be regarded as established that in a series of normal esters of secondary alcohols exhibiting optical activity, we may expect irregularities in the rotatory power to occur at the propionate, the n-valerate, and n-octoate and the n-decoate or undecoate, and that these irregularities are due to the fact that the ester chain of carbon atoms assumes a spiral form with about five atoms in one complete turn, entire turns being completed at the points of irregularity. That is to say, we recognise this phenomenon in two types of chain :

$$(a) \quad \frac{R^1}{R^2} \!\!>\!\! \underset{A}{CH \cdot O \cdot CO \cdot R} \quad \text{and} \quad (b) \quad \frac{R^1}{R^2} \!\!>\!\! CH \cdot O \cdot \overset{\prime\prime}{C}O \cdot R$$
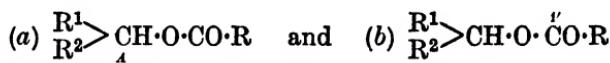
In type (a) when $R = 2, 7, 12$, and in type (b) when $R = 4, 9, 14$, one or more turns of the spiral to the right of the dotted line in the formulæ are completed with consequent effect on the rotatory power.

There are several objections, of course, to this thesis. In the present state of our knowledge, it is impossible to do more than indicate possible solutions of the difficulties. First, why should the spiral be counted up to the asymmetric carbon atom A in type (a) above, and only to the carbonyl carbon atom A' in type (b)—and, further, why not include the longest possible chain in the molecule for the purpose of counting atoms ? It is submitted that both the asymmetric carbon atom and the carbonyl carbon atom are singular points in the chain. They are secondary carbon atoms as distinct from the primary carbon atoms in the growing chain R. In view of the work of Ingold previously quoted on the variation of the intervalent angle of the carbon atom with the volume of the attached groups, and of the mathematical improbability of a spiral form being assumed by a chain of carbon atoms, it may well be that the introduction of a secondary carbon atom into a chain of primary carbon atoms already in a spiral form is sufficient to deflect the spiral, as it were, and to cause it thenceforward to assume an entirely different direction in space.

The second objection is much more serious. If it be true that

the normal form of the carbon chain is a spiral, then " straight-chain " compounds—for example, n-hexane, n-nonoic acid, n-dodecyl alcohol, should exist in enantiomorphous forms according as the spiral form assumed is left- or right-handed.   There should be the possibility of the existence of optically active substances the plane structural formulæ of which are symmetrical.   Why has this never been observed ?   It must be remembered that the phenomenon is more likely to be dynamic than static—the molecule cannot be assumed to be at rest in a permanently coiled-up form.   Whilst it may appear far-fetched to assume that the molecule is alternately coiling up and uncoiling, and then coiling up again in the opposite sense,* it is certainly a very significant fact that the spiral differs entirely from all asymmetric forms at present known to be associated with optical activity, in that it may, whilst still remaining in space of three dimensions, be converted into its mirror image without rupture. That is to say that a right-handed spiral may be converted into a left-handed one merely by straightening it out and then coiling it up in the opposite sense—no cutting of the chain is necessary. But to convert the generally accepted asymmetric molecule into its enantiomorph a much more drastic course is necessary.   Two of the groups attached to the " asymmetric " carbon atom must be removed, interchanged, and replaced in their new inverse order, thus involving more or less complete dismemberment of the molecule.

In addition to these stereochemical considerations, there are a few more or less isolated points of interest which will be touched on as briefly as possible.

d-β-*Butyl Formate*.—This is the simplest possible optically active ester of an organic acid.   Its rotatory power is high, thus supporting the claim that complicated molecular structure is not necessary for large rotations.   It will be noticed that the esters of β-butanol do not show irregularities of rotatory power at any point in the series, at least under the experimental conditions hitherto attained.

d-β-*Octyl Formate*.—The first lævorotatory ester of d-β-octanol to be described, if we except d-β-octyl 1-naphthoate (Part XII, p. 125), which exhibits lævorotation for λ = 4358 below 25°.   It is not a case of inversion, for d-β-octanol of full dextrorotatory power is obtained by hydrolysis of the strongly lævorotatory ester. Its temperature-rotation curves are similar to those of the acetate, etc., in that its lævorotation increases with rise of temperature,

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* It is not necessary, of course, that the coiling and uncoiling of the molecular chain should be rapid.   In the liquid or dissolved state, a statistical equilibrium would be set up which, if it were disturbed, would not require a very speedy equilibration in order to avoid detection of the disturbance by the methods of resolution at present at our disposal.

whilst in the case of the acetate, etc., the dextrorotation decreases with rise of temperature, that is to say, in all cases rise of temperature produces a change in rotatory power in the same sense.

d-γ-*Nonyl Formate.*—Like the other aliphatic esters of *d*-γ-nonanol, the formate is lævorotatory, but its rotation is numerically much greater. Its rotatory power varies scarcely at all with temperature and its temperature–rotation curves exhibit maxima (minima of lævorotatory power) which move towards a higher rotation value and a lower temperature value with decreasing wave-length. In this respect it resembles *d*-γ-nonyl acetate (Part VII, p. 2242).

d-*Benzylmethylcarbinyl Formate.*—This ester differs from the other aliphatic esters of the same alcohol in that it is lævorotatory. The temperature–rotation curves of all the esters are similar, however, just as in the case of the esters of *d*-β-octanol.

EXPERIMENTAL.

The esters were all prepared by the general method of condensing the appropriate optically active alcohol with anhydrous formic acid in the presence of zinc chloride. A considerable excess of the acid was employed in every case.

Anhydrous (98 *per cent.*) *Formic Acid.*—This was prepared by the convenient method of Maquenne (*Bull. Soc. chim.*, 1888, [ii], **50**, 662). Commercial (90 per cent.) formic acid was mixed with enough pure (98 per cent.) sulphuric acid to form the monohydrate, H_2SO_4,H_2O, with all the water present. The formic acid was distilled off in a vacuum and collected in a receiver cooled in ice-water, in which it solidified (m. p. of pure formic acid = 8°). By exercising care in mixing the acids and maintaining the temperature of the mixture below 70°, both during the mixing and during the distillation, the dehydration of the formic acid to carbon monoxide was reduced to a minimum.

d-β-*Butyl Formate*, $CHMeEt \cdot O \cdot CO \cdot H$.—*d*-β-Butanol (7·8 grams), formic acid (10 grams), and zinc chloride (8 grams) were heated on the water-bath for half an hour. At the end of that time, a slight odour of butylene was apparent. The reaction mixture was poured carefully into cold water, extracted with ether, and the ether extract washed repeatedly first with water, then with dilute aqueous sodium carbonate, and finally with water again. It was then dried by means of freshly ignited potassium carbonate, the ether was removed, and the ester distilled at atmospheric pressure through a fractionating column until its refractive index and rotatory power were unaltered by further distillation.

Thus prepared, *d*-β-butyl formate is a pleasant smelling, colourless, mobile liquid, b. p. 96—97°.

d-β-*Octyl Formate*, C_6H_{13}·CHMe·O·CO·H.—This ester was prepared by heating together d-β-octanol (13 grams), formic acid (9 grams), and zinc chloride (5 grams) on the water-bath for two hours. At the end of that time, the reaction mixture had separated into two layers. The ester was purified as in the preceding case except that it was distilled under reduced pressure and no column was used. d-β-Octyl formate is a fragrant, colourless, limpid liquid, b. p. 81—82°/20 mm. On hydrolysis with aqueous caustic soda in a current of steam, it yields optically pure d-β-octanol.

d-γ-*Nonyl Formate*, C_6H_{13}·CHEt·O·CO·H.—The preparation of this ester followed exactly the same course as that of the β-octyl ester, using d-γ-nonanol (15 grams), formic acid (9 grams), and zinc chloride (7 grams). It is a colourless, limpid liquid with a pleasant odour and boils at 94·5—95°/22 mm.

d-*Benzylmethylcarbinyl Formate*, C_6H_5·CH_2·CHMe·O·CO·H.—This ester was prepared by heating d-benzylmethylcarbinol (10 grams), formic acid (7 grams), and zinc chloride (6 grams) just as for the β-octyl and γ-nonyl formates. It is a mobile, highly refractive, colourless liquid, boiling at 108—110°/19 mm. Its odour is very penetrating but not unpleasant.

Density Determinations.

Densities were determined in a pyknometer holding about 3 c.c., except in the case of d-β-butyl formate, when one of about 1·5 c.c. capacity was used. The densities are calculated with reference to that of water at 4°.

d-β-*Butyl formate*.

$t°$	21·5°	45°	63°	94°
$d_{4°}^{t°}$	0·8820	0·8580	0·8364	0·8007

d-β-*Octyl formate*.

$t°$	12·5°	51°	73°	99°	134°
$d_4^{t°}$	0·8718	0·8397	0·8196	0·7954	0·7591

d-γ-*Nonyl formate*.

$t°$	20°	41°	55°	84·5°	107°	130°	154°
$d_{4°}^{t°}$	0·8688	0·8509	0·8390	0·8153	0·7941	0·7778	0·7536

d-*Benzylmethylcarbinyl formate*.

$t°$	22°	42°	73°	100°	127°	152°
$d_4^{t°}$	1·027	1·008	0·9800	0·9572	0·9324	0·9099

Refractive Index Determinations.

Refractive indices were determined in a Pulfrich refractometer with jacketed optical parts. Water from a thermostat was pumped round the jacket to ensure temperature control to 0·1°. Mono-chromatic light of five wave-lengths was employed (wave-lengths

are measured in Å.U.). The molecular refractive powers of the compounds are calculated using the Lorenz-Lorentz formula, and are compared with the values obtained by using Eisenlohr's figures for the atomic refractive powers of their constituent elements.

d-β-*Butyl formate.*

λ	6708	5896	5790	5461	4358
$n_\lambda^{25.3°}$	1·3786	1·3812	1·3817	1·3828	1·3896

$[R_L]_{5896}^{25.1°}$ observed 26·97 ⎫ Δ — + 0·03
calculated 26·94 ⎭

d-β-*Octyl formate.*

$n_{5896}^{12.5°}$ 1·4174

$[R_L]_{5896}^{12.5°}$ observed 45·64 ⎫ Δ = + 0·22
calculated 45·42 ⎭

d-γ-*Nonyl formate.*

λ	6708	5896	5790	5461	4358
$n_\lambda^{25.6°}$	1·4152	1·4182	1·4178	1·4196	1·4271

$[R_L]_{5896}^{25.6°}$ observed 50·14 ⎫ Δ = + 0·11
calculated 50·03 ⎭

d-*Benzylmethylcarbinyl formate.*

λ	6708	5896	5790	5461	4358
$n_\lambda^{24.5°}$	1·4930	1 4975	1 4982	1·5009	1·5251

$[R_L]_{5896}^{24.5°}$ observed 46·92 ⎫ Δ = + 0·49
calculated 46·43 ⎭

Measurements of Rotatory Power.

The rotatory powers of the esters were measured in a 50 mm. jacketed tube round which heated mineral oil was circulated by means of a small rotary pump. The temperature of the active liquid was kept constant within 0·5° for each observation.

Table I gives the experimentally observed rotations for the 50 mm. tube. When these rotations are plotted against the corresponding temperatures, smooth curves are obtained from which the values of the rotatory power at temperature intervals of 20° were calculated. These values are collected in Table II.

TABLE I.

The observed rotatory powers of the esters in the homogeneous state.

The measurements refer to a 50 mm. tube.

d-β-*Butyl formate.*

α_{5893} + 8·47° at 17°; 7·87° at 28°; 7·01° at 45°; 6·48° at 54°; 6·16° at 63°; 5·02° at 94°.

α_{5461} 10·12° at 17°; 9·16° at 32°; 8·45° at 45°; 7·83° at 56·5°; 7·32° at 65°; 5·96° at 94°.

α_{4358} 16·58° at 17°; 15·00° at 32°; 13·80° at 45°; 12·70° at 55·5°; 11·42° at 69°; 9·80° at 94°.

TABLE I.—(*continued*).

d-β-*Octyl formate.*

a_{5893} — 1·72° at 16°; — 2·22° at 37°; — 2·41° at 47·5°; — 2·89° at 71°;
— 3·36° at 101°; — 3·54° at 126·5°; — 3·59° at 149°.
a_{5461} — 2·14° at 16°; — 2·62° at 38°; — 3·04° at 52°; — 3·47° at 70°;
— 4·14° at 99°; — 4·38° at 126·5°; — 4·48° at 146°.
a_{4358} — 4·11° at 16°; — 5·12° at 38·5°; — 5·54° at 49°; — 6·27° at 71°;
— 7·18° at 100·5°; — 7·73° at 129°; — 7·95° at 145·5°.

d-γ-*Nonyl formate.*

a_{5893} — 4·89° at 17°; — 4·80° at 50°; — 4·65° at 65°; — 4·50° at 92°;
— 4·45° at 118°.
a_{5461} — 5·83° at 17°; — 5·63° at 47°; — 5·47° at 67°; — 5·44° at 72°;
— 5·27° at 93°; — 5·21° at 120°.
a_{4358} — 10·23° at 17°; — 9·94° at 44°; — 9·69° at 70°; — 9·63° at 79°;
— 9·53° at 93°; — 9·44° at 119°.

d-*Benzylmethylcarbinyl formate.*

a_{5893} — 2·36° at 15°; — 2·56° at 31°; — 2·74° at 57°; — 3·05° at 89°;
— 3·15° at 105°; — 3·32° at 124°.
a_{5461} — 2·76° at 15°; — 3·04° at 30°; — 3·50° at 58°; — 3·75° at 80°;
— 4·03° at 99°; — 4·23° at 113°; — 4·28° at 124°.
a_{4358} — 5·42° at 15°; — 5·83° at 31°; — 6·01° at 42°; — 6·73° at 65°;
— 6·92° at 76°; — 7·58° at 110°; — 7·96° at 125°.

TABLE II.

The specific rotatory powers of the esters in the homogeneous state.

d-β-*Butyl formate* (Mol. Wt. = 102).

$t°$.	$D_4^{t°}$.	$[a]_\lambda^{t°}$ 5893.	5461.	4358.
20	0·8846	+18·74°	+22·48°	+36·76°
40	0·8621	16·87	20·27	33·06
60	0·8391	15·04	18·19	29·31
80	0·8163	13·48	16·19	26·28

d-β-*Octyl formate* (Mol. Wt. = 158).

$t°$.	D_4^t.	$[a]_\lambda^{t°}$ 5893.	5461.	4358.
20	0·8658	−4·16°	−5·04°	−9·93°
40	0·8490	5·35	6·43	12·20
60	0·8313	6·45	7·84	14·29
80	0·8130	7·45	9·15	16·16
100	0·7941	8·36	10·38	18·01
120	0·7746	9·04	11·25	19·45
140	0·7540	9·47	11·83	20·87

d-γ-*Nonyl formate* (Mol. Wt. = 172).

$t°$.	$D_4^{t°}$.	$[a]_\lambda^{t°}$ 5893.	5461.	4358.
20	0·8688	−11·28°	−13·47°	−23·48°
40	0·8518	11·27	13·36	23·42
60	0·8349	11·26	13·24	23·42
80	0·8181	11·24	13·13	23·52
100	0·8011	11·23	13·11	23·72
120	0·7842	11·25	13·26	24·08

d-*Benzylmethylcarbinyl formate* (Mol. Wt. = 164).

$t°$.	$D_4^{t°}$.	$[a]_\lambda^{t°}$ 5893.	5461.	4358.
20	1·0276	−4·73°	−5·57°	−10·80°
40	1·0098	5·15	6·34	11·97
60	0·9919	5·58	7·06	13·18
80	0·9742	6·04	7·78	14·39
100	0·9563	6·48	8·45	15·58
120	0·9385	6·99	9·12	16·64

TABLE III.

The rotatory powers of the esters in approximately five per cent. solutions.

Ester.	Solvent.	$t°$.	Weight of ester in grams in 100 c.c. of solution.	α obs. 2-dcm.			$[\alpha]\lambda$.		
				5893.	5461.	4358.	5893.	5461.	4358.
d-β-Butyl formate	Carbon disulphide	18·5	4·85	+ 0·95°	+ 1·09°	+ 1·61°	+ 9·8°	+ 11·2°	+ 16·6°
	Ethyl alcohol	,,	4·97	+ 2·01	+ 2·25	+ 3·80	+ 20·2	+ 22·7	+ 38·3
d-β-Octyl formate	Carbon disulphide	lab. temp.	5·82	− 2·19	− 2·57	− 4·75	− 18·8	− 22·1	− 40·8
	Ethyl alcohol	,,	6·73	− 0·73	− 0·99	− 1·70	− 5·4	− 7·3	− 12·6
	Pyridine	,,	4·07	− 0·94	− 1·08	− 1·85	− 11·5	− 13·3	− 22·7
	Acetone	,,	4·83	− 0·61	− 0·70	− 1·13	− 6·3	− 7·2	− 11·7
d-γ-Nonyl formate	Carbon disulphide	17·5	5·48	− 2·29	− 2·70	− 4·90	− 20·9	− 24·6	− 44·7
	Ethyl alcohol	18·5	5·06	− 1·37	− 1·54	− 2·71	− 13·5	− 15·2	− 26·8
d-Benzylmethyl-carbinyl formate	Carbon disulphide	17·0	5·40	− 1·65	− 2·05	− 4·05	− 15·3	− 19·0	− 37·5
	Ethyl alcohol	,,	5·58	− 0·15	− 0·16	− 0·45	− 1·3	− 1·4	− 3·9

The rotatory powers of the esters were also measured in approximately 5 per cent. solution in carbon disulphide and in ethyl alcohol. For this purpose, approximately one gram of active substance was made up to 20 c.c. with the solvent, and the rotatory power of the solution determined in a 200 mm. tube. These results are given in Table III.

II.—*Investigations on the Dependence of Rotatory Power on Chemical Constitution. Part XIV. The Normal Aliphatic Ethers of* d-β-*Octanol.*

By JOSEPH KENYON and REGINALD ARTHUR McNICOL.

IN the preceding parts of this series of investigations the optical rotatory and rotatory dispersive powers of a considerable number of secondary alcohols and of esters derived from them have been examined. From the results obtained three main conclusions may be drawn.

(1) In a homologous series of optically active alcohols of the general formula $R \cdot CH(OH) \cdot R^1$, where R represents the growing aliphatic chain, departures from what may be termed the normal alteration of rotatory power with increase of molecular weight are observed when R consists of a chain of five or ten (eleven) carbon atoms.

(2) A similar phenomenon is observed in homologous series of esters of the formula $R^1 R^2 \cdot CH \cdot O \cdot CO \cdot R$ when the growing chain R contains five or ten (eleven) carbon atoms. It will be noticed that this case differs from (1) above in that R is not directly attached to the asymmetric carbon atom.

(3) Alcohols of simple chemical constitution possess simple rotatory dispersive powers under widely varying conditions of temperature, whereas the aliphatic esters derived from them show simple rotatory dispersive powers only at low temperatures; at higher temperatures and in solution the dispersive powers become complex.

The results obtained by observing the rotatory powers of these two classes of compound, both in the homogeneous state over a wide range of temperature and in solution at the temperature of the laboratory, make it highly probable that the differences in

dispersive power are due to some change in the molecular constitution of the esters occurring with change of conditions, and it has been suggested that this phenomenon may be due to some specific property of the carboxylic portion of the molecule.

In view of the possible effect of adjacent oxygen atoms in the carboxylic portion of the molecule, it was thought advisable to examine the rotatory powers of substances in which this possible disturbing factor is not present. To this end, a series of ethers was prepared containing in each case, as the asymmetric portion of the molecule, the sec.-octyl radicle, and, as the second radicle, one of the normal alkyl groups methyl, ethyl, up to n-nonyl. Such a series of compounds seems to fulfil the conditions laid down above. sec.-Octyl alcohol was chosen as the parent alcohol because it is the most readily obtainable of the optically active alcohols of simple chemical constitution.

The investigation of the optical properties of these ethers has led to the following interesting results—at all temperatures between 15° and 130° they exhibit simple rotatory dispersion, for at no point within these limits does the dispersion ratio $\alpha_{4358}/\alpha_{5461}$ fall below the value 1·577, and, in addition, when the reciprocal of the rotation is plotted against the square of the wave-length of the light used, linear curves are obtained for every ether examined, showing that the one-term Drude equation expresses the relation between rotatory power and wave-length of the light used.

Determinations of the rotatory powers of the ethers in the homogeneous state over a range of temperatures 15—130° for light of different wave-lengths show the presence of marked depressions in the optical rotatory power in the case of the members containing the n-propyl, n-amyl and hexyl, and n-octyl radicle.

It is considered that these investigations show that the magnitude of the rotatory power may be influenced by the approximate closing of the spiral arrangement of three types of chain present in all these compounds. These are (a) any complete chain through the molecule, (b) the chain of atoms up to and including the asymmetric carbon atom, and (c) the chain of atoms attached to the asymmetric carbon atom. In the case of the secondary alcohols dealt with in the earlier parts of these investigations, conclusive evidence has been obtained that the rotatory power is affected at intervals not only by the chain of the whole molecule, but also by the chain attached to the asymmetric carbon atom, whilst in the case of the esters of these alcohols as shown in Part XIII (this vol., p. 1) the influence of chains of the types (b) and (c) is demonstrated. In the case of the ethers herein described, the evidence is not conclusive, but points to the possi-

bility that the magnitudes of the rotatory powers of different members of the series are affected by the completion of a spiral in chains of all three types.

The irregularities due to this cause may be most clearly demonstrated by plotting rotatory powers as ordinates against the number of carbon atoms in the growing chain as abscissæ.   In the figure,

FIG. 1.
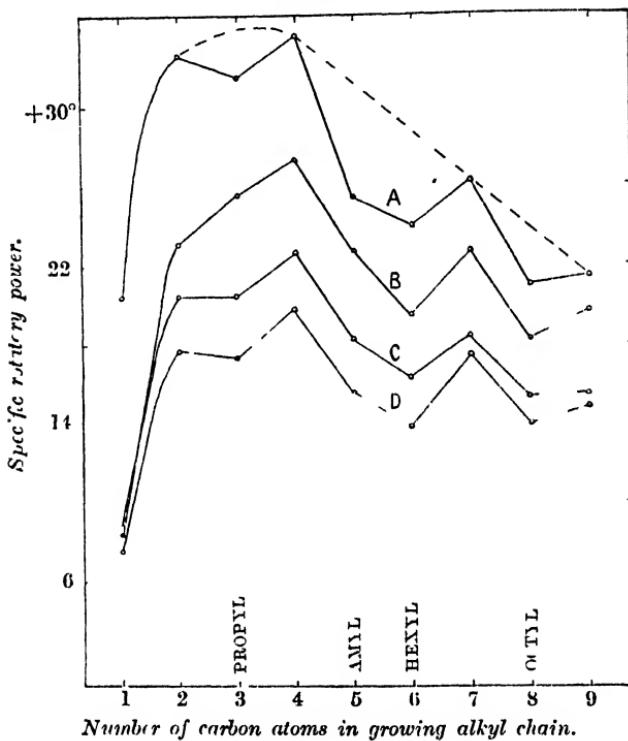
The ethers of d-β-Octanol.

A. $[\alpha]_{5461}$ in 5% solution in carbon disulphide.
B. $[\alpha]_{4358}^{120}$ in the homogeneous state.
C. $[\alpha]_{5461}^{0}$,,   ,,   ,,   ,,
D. $[\alpha]_{5461}$ in 5% solution in ethyl alcohol.

the values actually plotted are for $[\alpha]_{5461}$, but strictly similar curves are obtained by plotting the specific rotatory powers for any of the wave-lengths employed.

A very unusual effect was observed when the rotations of these ethers were determined in 5 per cent. solutions in carbon disulphide and in ethyl alcohol; in all previous cases in this series of investigations, it has been found that the former solvent effects a consider-

able depressing action, and the latter solvent an exalting action, although to a less degree.   In the series of ethers now being considered, however, the reverse is the case, for carbon disulphide causes enhanced rotations and ethyl alcohol depressed ones.   As may be seen from the diagram, the deviations from what may be regarded as the normal values are the same in solution as for the substances in the homogeneous state.

The ethers may be prepared either according to the method of Ferns and Lapworth (T., 1912, **101**, 273), in which potassium β-octyloxide is added to a *n*-alkyl *p*-toluenesulphonate, or by allowing potassium β-octyloxide to react with a normal alkyl haloid.   Samples of an ether prepared by either method are identical in rotatory power, and this fact allows of a strong presumption that no racemisation occurs during either process.

EXPERIMENTAL.

Action of Potassium on d-β-*Octanol.*—To clean potassium (4 grams) covered with dry benzene (or dry ether) there was added slowly *d*-β-octanol (23 grams) at such a rate that the reaction did not become too vigorous; when most of the potassium had dissolved, the reaction was completed by gentle warming.   The reaction mixture was then poured into ice-water in an atmosphere of carbon dioxide, and the whole distilled in a current of steam. The distillate was extracted with ether, the ethereal extract dried and, after removal of ether and benzene, distilled under reduced pressure.   The octyl alcohol thus obtained showed $\alpha_{5461}^{16°} + 19\cdot36°$ in a 2-dcm. tube, whereas the original alcohol showed $\alpha_{5461}^{16°} + 19\cdot40°$. Thus it is evident that no racemisation occurs under these conditions.

General Method of Preparation of the Optically Active Ethers.

To the solution (or suspension) of potassium β-octyloxide in ether (or benzene) was added the theoretical amount (calculated on the potassium used) of the alkyl bromide (or iodide), and the reaction mixture gently heated under reflux for about twenty hours, care being taken to prevent the access of moisture during this period. In the cases of methyl and ethyl iodides and ethyl bromide reacting with an ethereal solution of potassium β-octyloxide, heating is not necessary, standing at the ordinary temperature for several hours being quite sufficient.   The potassium bromide (or iodide) was washed out with water, and the dried ethereal (or benzene) solution mixed with sufficient phthalic anhydride to convert unchanged *sec*-octyl alcohol into its hydrogen phthalic ester.   After removing the ether (or benzene), the residue was heated at 110—115° for

<div align="center">

TABLE I.

</div>

*Determinations of Density $(D_4^{t^\circ})$ and of Rotatory Power $(\alpha_{50mm.})$
for the Ethers in the Homogeneous State.*

Methyl d-sec.-octyl ether.

$D_4^{t^\circ}$ 0·8076 at 19°; 0·7870 at 43·4°; 0·7700 at 62°; 0·7536 at 81·4°; 0·7391
at 99·4°.

α_{6438} 2·67° at 14°   2·07° at 53°; 1·85° at 61°; 1·55° at 81·5°; 1·36° at 101°.
α_{5461} 3·57° at 14°   2·70° at 51·4°; 2·67° at 61°; 2·33° at 82°; 1·86° at 104°.
α_{5086} 4·29° at 14°   3·24° at 53·5°; 3·16° at 61°; 2·65° at 81·5°; 2·43° at 98°.
α_{4800} 4·81° at 14°   3·56° at 54°; 3·54° at 61°; 3·09° at 81°; 2·83° at 98°.
α_{4678} 5·06° at 14°   3·75° at 55°; 3·70° at 61°; 3·22° at 81·5°; 3·00° at 98°
α_{4358} 5·87° at 14°; 4·60° at 51°; 4·18° at 61°; 3·76° at 82°; 3·22° at 98°.

Ethyl d-sec.-octyl ether.

$D_4^{t^\circ}$ 0·7895 at 17·2°; 0·7719 at 39·7°; 0·7545 at 58·5°; 0·7387 at 79·0°;
0·7202 at 100·5°.

α_{6438} 5·86° at 17·8°; 4·94° at 56°; 4·53° at 81°; 4·15° at 96°; 3·89° at 113°.
α_{5461} 8·08° at 17·8°; 6·97° at 54°; 6·24° at 79°; 5·68° at 97°; 5·47° at 110°.
α_{5086} 9·61° at 17·8°; 8·04° at 56°; 7·30° at 81°; 6·69° at 97°; 6·31° at 112°.
α_{4800} 10·47° at 17·8°; 9·10° at 55·5°; 8·29° at 80°; 7·56° at 95°; 7·12° at 112°.
α_{4678} 11·31° at 17·8°; 9·65° at 55°; 8·69° at 79°; 7·99° at 95°; 7·50° at 110°.
α_{4358} 13·09° at 17·8°; 11·19° at 54°; 10·04° at 79°; 9·19° at 95°; 8·81° at 105°.

n-Propyl d-sec.-octyl ether.

$D_4^{t^\circ}$ 0·7971 at 12°; 0·7598 at 61°; 0·7435 at 80°; 0·7303 at 96°.

α_{5461} 8·30° at 16·5°; 7·27° at 50·5°; 6·76° at 67°; 6·10° at 97°; 5·61° at 121°.
α_{4358} 13·42° at 16·5°; 11·70° at 50·5°; 10·97° at 67°; 9·77° at 96°; 9·12°
at 120°.

n-Butyl d-sec.-octyl ether.

$D_4^{t^\circ}$ 0·7971 at 18·5°; 0·7766 at 45°; 0·7568 at 70°; 0·7226 at 103°; 0·7063
at 135°.

α_{6438} 6·62° at 20°; 5·64° at 56°; 5·24° at 74°; 4·75° at 102°; 4·47° at 119°.
α_{5461} 8·94° at 20°; 7·75° at 57°; 7·18° at 76°; 6·70° at 98°; 6·05° at 118°.
α_{5086} 10·41° at 20°; 8·88° at 59°; 8·41° at 75°; 7·66° at 101°; 7·10° at 119°.
α_{4830} 11·82° at 20°; 9·98° at 59°; 9·20° at 75°; 8·59° at 101°; 7·89° at 119°.
α_{4678} 12·34° at 20°; 10·60° at 58°; 9·80° at 76°; 9·21° at 99°; 8·38° at 119°.
α_{4358} 14·38° at 20°; 12·16° at 57°; 11·37° at 76°; 10·62° at 98°; 9·69° at 118°.

n-Amyl d-sec.-octyl ether.

$D_4^{t^\circ}$ 0·7989 at 20°; 0·7820 at 42·5°; 0·7696 at 60°; 0·7484 at 84·4°; 0·7233
at 114·8°; 0·7023 at 139·6°.

α_{6438} 5·25° at 17°; 4·91° at 35°; 4·61° at 53°; 4·18° at 76°; 4·00° at 101°;
3·50° at 135°.
α_{5461} 7·38° at 17°; 6·94° at 35°; 6·34° at 54°; 5·90° at 72°; 5·41° at 105°;
4·97° at 135°.
α_{5086} 8·47° at 17°; 8·19° at 32°; 7·57° at 53°; 6·92° at 77·5°; 6·44° at 100°;
5·73° at 129°.
α_{4800} 9·63° at 17°; 9·17° at 31°; 8·57° at 54°; 7·84° at 77·5°; 7·33° at 100°;
6·58° at 130°.
α_{4678} 10·23° at 17°; 9·62° at 30°; 8·92° at 56°; 8·19° at 70°; 7·64° at 100°;
6·93° at 131°.
α_{4358} 11·79° at 17°; 11·08° at 35°; 10·33° at 54°; 9·50° at 74°; 8·75° at 102°;
7·85° at 133°.

TABLE I.—(continued).

n-Hexyl *d-sec.*-octyl ether.

$D_4^{t°}$ 0·8047 at 17·0°; 0·7881 at 40·4°; 0·7723 at 62·0°; 0·7568 at 82·5°; 0·7149 at 137°.

a_{6438} 4·69° at 21·2°; 4·29° at 42°; 3·77° at 80°; 3·39° at 108°; 2·98° at 137°.
a_{5461} 6·52° at 21·2°; 6·02° at 41°; 5·41° at 78°; 4·77° at 109°; 4·17° at 138°.
a_{5086} 7·48° at 21·2°; 6·96° at 42°; 6·17° at 80°; 5·59° at 106°; 4·88° at 137°.
a_{4800} 8·45° at 21·2°; 7·87° at 42°; 6·92° at 80°; 6·26° at 107°; 5·60° at 136°.
a_{4678} 8·89° at 21·2°; 8·33° at 42°; 7·26° at 79°; 6·46° at 108°; 5·87° at 135°.
a_{4358} 10·37° at 21·2°; 9·67° at 42°; 8·34° at 78°; 7·51° at 108°; 6·56° at 138°.

n-Heptyl *d-sec.*-octyl ether.

$D_4^{t°}$ 0·8034 at 22°; 0·7776 at 59°; 0·7672 at 73°; 0·7440 at 101°; 0·7290 at 125°.

a_{6438} 5·38° at 16°; 4·81° at 42°; 4·42° at 64°; 4·20° at 85°; 3·88° at 117°.
a_{5461} 7·50° at 16°; 6·81° at 43°; 6·47° at 61°; 5·99° at 85°; 5·49° at 121°.
a_{5086} 8·81° at 16°; 8·02° at 42°; 7·29° at 66°; 6·80° at 85°; 6·18° at 118°.
a_{4800} 9·81° at 16°; 9·09° at 43°; 8·38° at 63°; 7·90° at 83°; 7·09° at 118°.
a_{4678} 10·49° at 16°; 9·48° at 44°; 8·89° at 64°; 8·49° at 80°; 7·23° at 119°.
a_{4358} 12·09° at 16°; 10·87° at 45°; 10·18° at 64°; 9·50° at 82°; 8·41° at 120°.

n-Octyl *d-sec.*-octyl ether.

D_4^{t} 0·8099 at 15°; 0·7929 at 43°; 0·7780 at 65°; 0·7459 at 109°; 0·7254 at 143°.

a_{6438} 4·36° at 20°; 4·01° at 42°; 3·75° at 60°; 3·07° at 108°; 2·87° at 130°.
a_{5461} 6·20° at 20°; 5·59° at 43°; 5·16° at 61°; 4·35° at 108°; 4·22° at 130°.
a_{5086} 7·10° at 20°; 6·51° at 42°; 6·01° at 61°; 5·00° at 108°; 4·79° at 130°.
a_{4800} 8·05° at 20°; 7·35° at 42°; 6·68° at 62°; 5·54° at 108°; 5·37° at 130°.
a_{4678} 8·39° at 20°; 7·58° at 43°; 6·97° at 62°; 5·81° at 109°; 5·57° at 130°.
$a_{43.8}$ 9·98° at 20°; 8·92° at 44°; 8·36° at 62°; 6·80° at 105°; 6·59° at 125°.

n-Nonyl *d-sec.*-octyl ether.

$D_4^{t°}$ 0·8110 at 17°; 0·7911 at 47°; 0·7747 at 66°; 0·7573 at 89°; 0·7409 at 110°.

a_{6438} 4·49° at 20°; 4·17° at 45°; 3·72° at 75°; 3·48° at 97°; 3·30° at 116°.
a_{5461} 6·13° at 20°; 5·77° at 44°; 5·19° at 75°; 4·86° at 95°; 4·54° at 118°.
a_{5086} 7·27° at 20°; 6·62° at 46°; 6·10° at 75°; 5·66° at 96°; 5·39° at 117°.
a_{4800} 8·18° at 20°; 7·50° at 46°; 6·74° at 75°; 6·29° at 95°; 5·93° at 117°.
a_{4678} 8·63° at 20°; 8·96° at 45°; 7·05° at 76°; 6·71° at 93°; 6·21° at 115°.
a_{4358} 9·97° at 20°; 9·19° at 44°; 8·27° at 76°; 7·86° at 92·5°; 7·37° at 115°.

ten hours. The cold reaction product was dissolved in ether, extracted with dilute sodium carbonate solution, dried, the ether evaporated, and the resulting β-octyl alkyl ether purified by distillation under reduced pressure. In no case was any evidence obtained of the presence of unsaturated compounds. The sodium carbonate washings, after acidification, gave *d*-β-octyl hydrogen phthalate of the usual rotatory power.

Preparation of Ethyl d-sec.-*Octyl Ether by the Use of Ethyl* p-*Toluenesulphonate.*

The procedure described by Ferns and Lapworth (*loc. cit.*) was closely followed. Potassium *d*-β-octyloxide in benzene solution was allowed to react with the calculated amount of ethyl *p*-toluene-

TABLE II.

Physical Properties of Ethers of d-β-Octanol.

Ether.	B. p. °C. mm.	d_4^{25}.	n_D^{25}.	Molecular refractive power.		n_{6438}^{25}.	n_{5461}^{25}.	n_{4385}^{25}.	Refractive dispersive power.
				Found.	Diff. from calc. value.				
Methyl	76—77°/44	0·8094	1·4212	45·27	− 0·13	1·4202	1·4232	1·4317	0·02709
Ethyl	63—65/14	0·7861	1·4136	50·11	+ 0·07	1·4119	1·4156	1·4233	0·02721
n-Propyl	76/18	0·7887	1·4148	54·59	− 0·05	—	1·4173	1·4245	—
n-Butyl	85—86/14	0·7923	1·4168	59·32	+ 0·07	1·4146	1·4188	1·4255	0·02614
n-Amyl	99/15	0·7958	1·4218	63·84	− 0·03	1·4199	1·4236	1·4309	0·02598
n-Hexyl	115/15	0·7983	1·4252	68·65	− 0·13	1·4232	1·4269	1·4345	0·02644
n-Heptyl	129.18	0·8017	1·4267	72·98	− 0·13	1·4244	1·4280	1·4356	0·02633
n-Octyl	146.13	0·8038	1·4301	77·87	+ 0·11	1·4283	1·4319	1·4404	0·02643
n-Nonyl	163/18	0·8042	1·4325	82·61	− 0·16	1·4307	1·4344	1·4422	0·02654

TABLE III.

Comparison of Specific Rotatory Powers at 20° and 120°.

Ether.	$[\alpha]_\lambda^{20°}$						$[\alpha]_\lambda^{120°}$					
	λ 6438.	λ 5461.	λ 5086.	λ 4800.	λ 4678.	λ 4358.	λ 6438.	λ 5461.	λ 5086.	λ 4800.	λ 4678.	λ 4358.
Methyl	6·42	8·63	10·20	11·66	12·23	13·79	3·02	4·52	5·80	6·70	7·18	8·35
Ethyl	14·68	20·33	24·13	26·95	28·46	32·86	10·79	14·73	17·15	19·54	20·32	23·04
n-Propyl	—	20·51	—	—	—	32·92	—	15·78	—	—	—	25·65
n-Butyl	16·63	22·46	26·13	29·64	31·01	36·13	12·34	17·61	19·61	21·88	23·19	27·32
n-Amyl	13·03	18·19	22·09	23·83	25·42	29·06	10·34	14·19	16·56	18·92	19·86	22·87
n-Hexyl	11·68	16·29	18·68	21·05	22·45	25·95	8·65	12·36	14·39	15·68	16·97	19·54
n-Heptyl	13·18	18·41	21·58	24·11	25·72	29·75	10·42	14·62	16·48	19·05	19·73	22·85
n-Octyl	10·80	15·33	17·59	19·96	20·84	24·77	7·95	11·29	12·88	14·47	14·98	18·11
n-Nonyl	10·98	15·45	18·41	20·26	21·35	24·60	8·98	12·43	14·52	15·96	16·70	19·82

TABLE IV.

Comparison of Specific Rotatory Powers in 5 per cent. Solution.

(1) In carbon disulphide solution at room temperature in a 20-cm. tube.

Ether.	Grams in 100 c.c.	Observed rotation.						[r]λ.					
		6438.	5461.	5086.	4800.	4678.	4358.	6438.	5461.	5086.	4800.	4678.	4358.
Methyl	4·97	1·52	2·03	2·42	2·79	2·89	3·57	12·31	20·44	24·31	28·10	29·10	35·95
Ethyl	4·73	2·34	3·15	3·91	4·42	4·62	5·62	24·27	32·68	41·50	45·85	47·93	58·16
n-Propyl ...	5·47	—	3·41	—	—	6·16	—	—	31·42	—	—	—	56·26
n-Butyl	4·56	2·19	3·08	3·61	4·18	4·44	5·27	24·58	33·79	39·60	45·86	48·71	57·81
n-Amyl	3·53	1·34	1·78	2·16	2·41	2·59	3·09	19·00	25·24	30·62	34·16	36·61	43·81
n-Hexyl	3·17	1·14	1·52	1·87	2·11	2·22	2·59	17·97	23·96	27·51	33·16	34·99	40·83
n-Heptyl ...	4·26	1·63	2·23	2·80	3·21	3·37	3·85	19·15	26·20	32·90	37·71	39·50	45·23
n-Octyl	3·41	1·10	1·43	1·77	1·99	2·05	2·42	16·14	20·00	25·98	29·20	30·09	35·52
n-Nonyl	3·30	—	1·42	—	—	—	2·47	—	21·50	—	—	—	27·40

(2) In absolute ethyl alcohol solution at room temperature in a 20-cm. tube.

Ether.	Grams in 20 cc.	Observed rotation.						[α]λ.					
		6438.	5461.	5086.	4800.	4678.	4358.	6438.	5461.	5086.	4800.	4678.	4358.
Methyl	3·92	0·50	0·59	0·70	0·73	0·79	0·96	6·37	7·52	8·92	9·30	10·07	12·24
Ethyl	4·95	1·38	1·75	2·20	2·51	2·63	2·97	13·94	17·68	22·22	25·35	26·57	30·00
n-Propyl ...	5·10	—	1·76	—	—	—	2·96	—	17·24	—	—	—	28·99
n-Butyl	4·53	1·42	1·80	2·18	2·44	2·54	3·03	15·67	19·86	24·06	26·93	28·03	33·36
n-Amyl	4·81	1·19	1·49	1·81	2·03	2·10	2·43	12·37	15·50	18·82	21·12	21·84	25·28
n-Hexyl	3·52	0·91	1·07	1·31	1·41	1·54	1·70	12·91	13·85	18·59	20·01	21·85	24·69
n-Heptyl ...	4·84	1·28	1·71	2·03	2·24	2·42	2·76	13·22	17·66	20·96	23·13	24·99	27·88
n-Octyl	2·93	0·60	0·81	0·92	1·04	1·08	1·30	10·26	14·02	15·73	17·78	18·46	21·37
n-Nonyl	4·21	—	1·26	—	—	—	1·99	—	14·97	—	—	—	26·35

sulphonate dissolved in benzene. The gelatinous precipitate which had formed during six hours' heating on the water-bath was removed by filtration, and the filtrate warmed with aqueous alkali, washed with water, dried, and fractionally distilled under diminished pressure. In this way there were obtained, by the use of 8 grams of potassium, 5·4 grams of ethyl d-sec.-octyl ether with a b. p. 65°/16 mm. and $\alpha^{19°}_{5461} + 8·03°$ for 100 mm. These figures are in very close agreement with those given by the ether prepared by the general method described above using either ethyl bromide or ethyl iodide.

All the ethers, which were obtained in yields of 50—60 per cent. of the theoretical, are colourless, mobile liquids. The lower members possess somewhat penetrating but not unpleasant odours; some of their physical constants are collected in Table II.

Measurements of the rotations of these substances in ethyl alcohol and carbon disulphide solution were made at room temperature and at approximately 5 per cent. concentration.

III.—*Investigations on the Dependence of Rotatory Power on Chemical Constitution. Part XV. Some* n-*Alkyl Ethers of* d-*Benzylmethylcarbinol.*

By HENRY PHILLIPS.

OF the optically active compounds which exhibit complex rotatory dispersion, the great majority contain the carboxyl group (or its equivalents, the carboalkyloxyl or the xanthogenic ester group) and therefore it has been suggested that complex rotatory dispersion may be a general property of the carboxyl group and may even be specifically due to the variable valency of the oxygen atoms contained in it.

It is accordingly of interest to examine other optically active compounds containing an oxygen atom in the molecule in order to test this point. In the earlier parts of these investigations it has been shown that most secondary alcohols under very varied conditions of temperature exhibit simple rotatory dispersion, whilst in Part XIV (this vol., p. 14) there is described a homologous series of nine optically active ethers, all of which show simple rotatory dispersion. An extension of the latter investigation appeared

desirable and accordingly a series of normal alkyl ethers of d-benzyl-methylcarbinol was prepared and examined, with results which are discussed and detailed in this paper. d-Benzylmethylcarbinol was chosen for this purpose because its rotatory power is high and only slightly influenced by temperature. It can also be obtained fairly readily in a state of optical purity (Part VI, T., 1914, **106**, 1115).

FIG. 1.

Number of carbon atoms in growing alkyl chain.
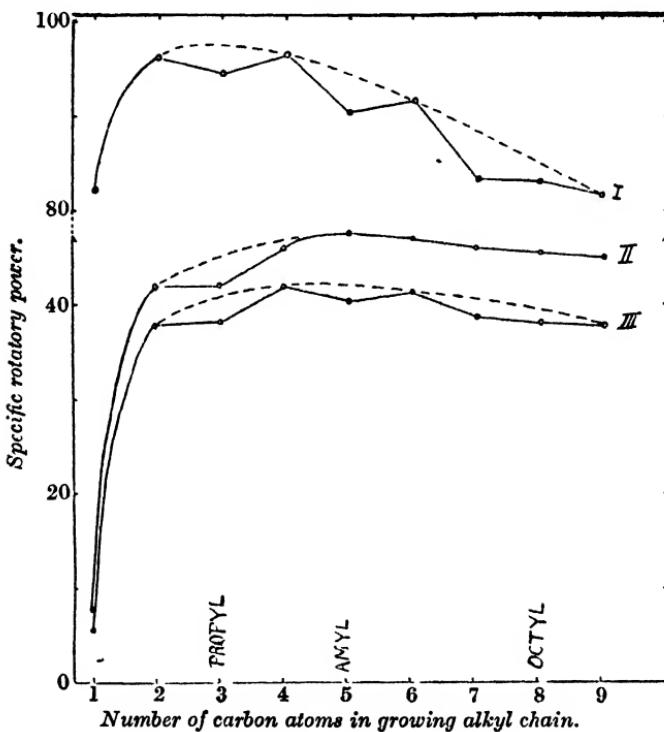
The Ethers of d-Benzylmethylcarbinol.

I. $[a]_{4358}$ in 5% solution in carbon disulphide.
II. $[a]_{4358}$ „ „ „ „ ethyl alcohol.
III. $[a]_{4358}^{100°}$ in the homogeneous state.

Nine members of the series $C_6H_5 \cdot CH_2 \cdot CH(CH_3) \cdot OR$, where R represents a normal alkyl group, have been prepared by the method described in Part XIV (*loc. cit.*) and shown to exhibit simple rotatory dispersion over the temperature range 20—140°.

Further support is thus afforded to the view that complex rotatory dispersion must be regarded as a property of the carboxyl group as a whole and not of any one atom in it. That is to say, it is to the propinquity of the oxygen atoms in this group that the equi-

librium $-C{<}{\overset{O}{\underset{OH}{}}} \rightleftharpoons -C{<}{\overset{O}{\underset{OH}{||}}}$, with consequent complexity of rotatory dispersion, is probably due. In alcohols, $R \cdot OH$, and ethers, $R \cdot O \cdot R^1$, it may be concluded that oxygen atoms in different molecules are not able to approach sufficiently near to each other to employ their subsidiary valencies, with the result that there is only one kind of molecule present in the substance, which therefore shows simple rotatory dispersion. This is well borne out by the fact that ethers and alcohols are known to associate only slightly if at all.

The magnitudes of the rotatory powers of the members of this series of ethers, as will be seen from Fig. 1, show remarkable irregularities. Assuming that the normal alteration of specific rotatory power with the growth of the alkyl chain is correctly indicated in the figure, it will be seen that depressions in the rotatory power occur at the propyl, amyl, heptyl, and octyl members. By analogy with previous results, the depressions at the propyl and octyl members are ascribed to the influence of the chain of five or ten atoms up to and including the asymmetric carbon atom, that at the heptyl member to the influence of the chain

$$CH_3 \cdot CH(CH_2Ph) \cdot O \cdot C_7H_{15},$$

whilst the depression at the amyl member,

$$CH_3 \cdot CH(CH_2Ph) \cdot O \cdot C_5H_{11},$$

is analogous to similar alteration in rotatory power exhibited by the valerates in some series of esters, as, for example,

$$CH_3 \cdot CH(C_6H_{13}) \cdot O \colon CO \cdot C_4H_9.$$
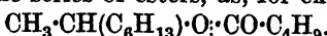
EXPERIMENTAL.

Preparation of d-*Benzylmethylcarbinol.*—The optically active alcohol required for this research was prepared by the method given in Part VI. One thousand six hundred and seventy grams of benzyl methyl ketone were obtained by the passage of 2660 grams of phenylacetic acid, dissolved in 11,450 grams of glacial acetic acid, through a silica tube heated at 400° and half filled with thoria. The ketone was reduced in boiling ethyl alcoholic solution by means of sodium to the corresponding alcohol, which was converted into the hydrogen phthalic ester. One thousand nine hundred grams of this ester were obtained, fractional crystallisation of the brucine salt of which from acetone yielded the pure *lBdA* salt. From this pure salt 230 grams of pure *d*-benzylmethylcarbinol were obtained. $d_4^{25^\circ} = 0.9877$; $n_{5896}^{25^\circ} = 1.5194$; $\alpha_{5461}^{16^\circ} + 32.76°$; $\alpha_{5461}^{20^\circ} + 33.22°$; $\alpha_{5461}^{31^\circ} + 33.28°$.

The yield of *lBdA* salt was diminished in the resolution by the crystallisation from the concentrated mother-liquors of the corre-

TABLE I.

n-Alkyl Ethers of d-Benzylmethylcarbinol.

	$D_4^{25°}$	Boiling point. °C/mm.	$n_\lambda^{25°}$ λ 6438.	λ 5896.	λ 5461.	λ 5086.	λ 4800.	λ 4678.	λ 4358.	$[R_L]_{5896}$ Observed λ=5896.	Diff. from calc.
Methyl	0·9314	85°/12	1·4875	1·4909	1·4942	1·4978	1·5015	1·5031	1·5082	46·67	+ 0·25
Ethyl	0·9162	93/19	1·4842	1·4875	1·4906	1·4942	1·4976	1·4994	1·5047	51·56	+ 0·49
Propyl	0·9093	103/13	1·4787	1·4818	1·4849	1·4874	1·4916	1·4933	1·4987	55·81	+ 0·15
Butyl	0·8991	115/12	1·4761	1·4791	1·4819	1·4854	1·4884	1·4900	1·4949	60·62	+ 0·34
Amyl	0·8900	127/14	—	1·4761	1·4787	—	—	·—	1·4913	65·35	+ 0·46
Hexyl	0·8878	137/14	—	1·4756	1·4783	—	—	—	1·4905	69·90	+ 0·39
Heptyl	0·8828	156/19	1·4722	1·4750	1·4778	1·4807	1·4837	1·4851	1·4895	74·69	+ 0·56
Octyl	0·8815	170/12	1·4720	1·4748	1·4775	1·4804	1·4832	1·4847	1·4892	79·25	+ 0·50
Nonyl	0·8820	126/1	—	1·4747	1·4773	—	—	—	1·4889	83·67	+ 0·30

sponding *lBlA* salt. Complicated mixtures of the two salts were obtained on recrystallisation, which, however, finally resulted in the isolation of a small quantity of almost pure *lBlA* salt. From this were isolated 6 grams of *l*-benzylmethylcarbinol, $\alpha_{5461}^{16°} - 30.90°$.

Action of Potassium on Benzylmethylcarbinol.—Fifteen grams of a partly active alcohol, with $\alpha_{5461}^{20°} - 6.13°$ in a 50 mm. tube, dissolved in 100 c.c. of dried benzene, were treated with 2 grams of powdered potassium. On complete dissolution of the metal, the *l*-alcohol was recovered. It had $\alpha_{5461}^{20°} - 6.09°$ in a 50 mm. tube.

General Method of Preparation of the Active Ethers.—Except for the use of 3 grams of potassium with 11 grams of the *d*-alcohol, dissolved in benzene, the method employed was the same as that given in Part XIV (*loc. cit.*). The yield was 30—40 per cent. of the theoretical.

The lower members of the series are pleasant-smelling liquids; the methyl and ethyl ethers have odours reminiscent of nerol.

In Table I are given some physical properties of the ethers, whilst in Table III are recorded the specific rotatory powers calculated from the observed rotatory powers given in Table II. The determinations of rotatory power in ethyl alcohol and in carbon disulphide are tabulated in Tables IV and V, respectively.

The densities were determined in a pyknometer holding about 3 c.c. The rotations were measured in 50 mm. tubes, round which heated mineral oil was circulated by means of a pump, but are here given as for 100 mm.

TABLE II.

Observations of Density ($D_4^{t°}$) *and Rotatory Power* ($\alpha_{100\ mm}$) *in the Homogeneous State of the* n-*Alkyl Ethers of* d-*Benzylmethylcarbinol.*

Methyl.

Density 0.9273 at 27°; 0.9135 at 47.5°; 0.8909 at 74.5°; 0.8718 at 96.3°;
    0.8550 at 112°; 0.8392 at 131.5°.

α_{6438} 4.34° at 18°; 4.20° at 29.5° *; 3.68° at 47.5°; 3.24° at 67°; 2.64° at
    88°; 2.04° at 109°.

α_{5461} 6.00° at 18°; 5.10° at 36.4° *; 4.76° at 47°; 4.18° at 62°; 3.50° at 83°;
    2.80° at 106°.

α_{5086} 7.32° at 18°; 6.68° at 28°; 5.88° at 47.5°; 4.92° at 65°; 3.88° at 88°;
    3.16° at 108°.

α_{4800} 8.34° at 18°; 7.92° at 27°; 6.82° at 47.5°; 5.80° at 63°; 4.62° at 88°;
    3.66° at 107°.

α_{4678} 8.80° at 18°; 8.28° at 26° *; 7.20° at 47.5°; 6.28° at 62.5°; 4.94° at
    87°; 4.00° at 106°.

α_{4358} 10.22° at 18°; 9.04° at 34° *; 6.96° at 61°; 6.26° at 70°; 5.52° at
    83.5°; 4.38° at 102°; 4.50° at 106°.

* While cooling.

TABLE II.—(continued).

Ethyl.

Density 0·9171 at 24°; 0·9068 at 36·5°; 0·8781 at 71·5°; 0·8510 at 101·5°; 0·8344 at 123°; 0·8145 at 144·5°.

a_{6438} 16·18° at 22°; 15·46° at 43°; 14·22° at 67°; 13·30° at 87·2°; 12·10° at 111° *; 11·42° at 133°.

a_{5461} 23·80° at 19°; 20·48° at 67°; 18·98° at 87°; 17·72° at 112°; 16·84° at 121°; 15·90° at 140°.

a_{5086} 27·60° at 22°; 26·20° at 43°; 24·44° at 67°; 22·64° at 87°; 21·10° at 111° *; 19·88° at 133°.

a_{4800} 32·02° at 22°; 30·46° at 43°; 28·40° at 67°; 26·52° at 87°; 24·30° at 113° *; 22·80° at 133°.

a_{4678} 34·38° at 22°; 32·28° at 43°; 30·42° at 67°; 28·22° at 87°; 26·16° at 113° *; 24·70° at 133°.

a_{4358} 41·00° at 19°; 38·14° at 44°; 35·92° at 67°; 32·92° at 87°; 30·58° at 112°; 28·24° at 131°.

n-Propyl.

Density 0·9058 at 28°; 0·8871 at 53°; 0·8662 at 78°; 0·8486 at 99°; 0·8342 at 114°; 0·8312 at 120°.

a_{6438} 16·10° at 23°; 15·34° at 45°; 14·62° at 60°; 14·42° at 70° *; 13·96° at 81°; 13·26° at 95·5°; 12·66° at 111°.

a_{5461} 23·52° at 22°; 22·16° at 45°; 20·86° at 62°; 20·22° at 72° *; 19·72° at 81°; 18·86° at 94°; 17·98° at 111°.

a_{5086} 27·74° at 23°; 26·32° at 45°; 24·98° at 60·5°; 24·26° at 70·4° *; 23·38° at 81°; 22·36° at 95°; 21·62° at 110·5°.

a_{4800} 31·78° at 23°; 30·06° at 45°; 28·42° at 61°; 27·72° at 71° *; 26·86° at 81°; 25·66° at 95°; 24·68° at 111°.

a_{4678} 33·80° at 23°; 32·00° at 45°; 29·98° at 62°; 28·34° at 80°; 27·04° at 94·5°; 26·16° at 110°.

a_{4358} 40·50° at 23°; 37·76° at 45°; 36·08° at 61·5°; 34·70° at 72° *; 33·88° at 81°; 32·54° at 94°; 30·98° at 110·5°.

n-Butyl.

Density 0·8973 at 27°; 0·8857 at 43°; 0·8686 at 65°; 0·8528 at 84°; 0·8308 at 112°.

a_{6438} 17·46° at 21°; 16·78° at 45°; 16·02° at 60·5°; 15·52° at 77°; 14·64° at 94°; 14·32° at 104·5° *; 13·66° at 121°.

a_{5461} 24·94° at 21·5°; 23·96° at 43°; 22·40° at 63°; 21·68° at 75·5°; 20·20° at 98°; 19·88° at 105·5°; 19·26° at 118°.

a_{5086} 34·18° at 21°; 32·40° at 45°; 30·54° at 61·5°; 29·54° at 77°; 28·04° at 96°; 27·28° at 105°; 26·30° at 120°.

a_{4800} 29·76° at 21°; 28·24° at 45°; 26·74° at 61°; 25·72° at 77°; 24·46° at 94·5°; 23·82° at 104·5° *; 22·96° at 120°.

a_{4678} 35·86° at 21°; 34·10° at 44°; 32·32° at 62°; 31·14° at 77°; 29·44° at 96·5°; 28·62° at 105° *; 27·76° at 119°.

a_{4358} 43·36° at 22°; 38·54° at 62°; 37·08° at 75°; 35·98° at 84° *; 34·94° at 97·5°; 34·00° at 106°; 33·00° at 120°.

n-Amyl.

Density 0·8871 at 29°; 0·8777 at 42°; 0·8484 at 80°; 0·8301 at 102°; 0·8153 at 122°; 0·7994 at 141°.

a_{5892} 20·26° at 22°; 19·12° at 41°; 18·62° at 58°; 17·98° at 74°; 16·84° at 90°; 15·74° at 110°; 15·16° at 120°.

a_{5461} 24·00° at 20·5°; 22·72° at 41°; 21·98° at 57°; 21·32° at 73°; 19·88° at 93°; 19·36° at 106°; 18·06° at 120°.

a_{4358} 41·50° at 21°; 39·30° at 41°; 37·90° at 57°; 36·48° at 72°; 33·90° at 93°; 32·42° at 106°; 31·14° at 119°.

---

* While cooling.

TABLE II.—*(continued).*

n-Hexyl.

Density 0·8845 at 28·5°; 0·8742 at 43°; 0·8562 at 67°; 0·8420 at 86°; 0·8230 at 108°; 0·7990 at 140°.

a_{5893} 20·28° at 20·5°; 19·40° at 40°; 19·28° at 45·5°; 18·58° at 60°; 17·20° at 93°; 16·26° at 123°.

a_{5461} 24·08° at 20·5°; 22·80° at 40°; 21·64° at 59°; 20·68° at 74°; 19·70° at 98°; 19·26° at 111°; 18·58° at 122·5°.

a_{4358} 41·22° at 21°; 39·22° at 40°; 38·50° at 46°; 33·90° at 73·5°; 34·44° at 94°; 33·18° at 112°; 32·30° at 122·5°.

n-Heptyl.

Density 0·8816 at 27°; 0·8728 at 39°; 0 8430 at 82°; 0·8287 at 100°; 0·8167 at 116°; 0·8052 at 131·5°.

a_{6438} 16·00° at 19°; 15·20° at 43°; 14·44° at 60°; 13·36° at 88·5°; 13·04° at 111·5°; 12·18° at 134°.

a_{5461} 22·90° at 19°; 21·70° at 44°; 20·00° at 71°; 19·22° at 89°; 18·14° at 111°; 17·32° at 134°.

a_{5086} 26·98° at 19°; 25·48° at 44°; 24·00° at 62°; 22·78° at 88·5°; 21·52° at 111·5°; 20·32° at 134°.

a_{4800} 30·92° at 19°: 29·22° at 44°; 27·44° at 64°; 26·16° at 88°; 24·74° at 111°; 23·16° at 134°.

a_{4678} 32·68° at 19°; 30·98° at 44·5°; 29·02° at 67°; 27·78° at 88°; 26·34° at 111°;   24·58° at 134°.

a_{4358} 39·32° at 19°; 36·84° at 43°; 34·04° at 71°; 32·60° at 89°; 31·06° at 110·5°; 29·58° at 134°.

n-Octyl.

Density 0·8809 at 26°; 0·8700 at 41·5°; 0·8565 at 60°; 0·8397 at 84°; 0·8195 at 114°; 0·7981 at 142°.

a_{6438} 15·26° at 20·5°; 14·64° at 32°; 14·28° at 54°; 13·46° at 71·5°; 12·98° at 89°; 12·46° at 111·5°; 11·90° at 129°.

a_{5461} 22·08° at 20·5ᶜ; 21·50° at 32°; 20·68° at 51°; 19·50° at 71°; 18·56° at 93°; 17·68° at 109°; 17·18° at 126°.

a_{5086} 25·84° at 20·5°; 25·26° at 33°; 24·32° at 53°; 22·86° at 71°; 22·12° at 89°; 20·86° at 110°; 20·02° at 128·5°.

a_{4800} 29·70° at 20·5°; 29·08° at 33·5°; 27·94° at 58·4°; 26·54° at 70°; 25·30° at 90°; 24·04° at 109°; 23·10° at 128 2°.

a_{4678} 31·54° at 20·5°; 30·82° at 35°; 29·56° at 51·6°; 28 10° at 69°; 26·78° at 90·5°; 25·52° at 107°; 24·42° at 127°.

a_{4358} 37·44° at 21°; 36·82° at 32°; 35·26° at 51°; 33·08° at 77°; 31·52° at 93°; 30·42° at 109·5°; 28·84° at 126°.

n-Nonyl.

Density 0·8822 at 25°; 0·8688 at 44°; 0·8561 at 63°; 0·8377 at 87·5°; 0·8128 at 122°; 0·7989 at 143°.

a_{5893} 18·32° at 21°; 17·68° at 37·5°; 16·40° at 66°; 15·96° at 85·5°; 15·46° at 98·5°; 15·10° at 111°*; 14·94° at 122°.

a_{5461} 21·88° at 21°; 21·10° at 38°; 20·34° at 49°; 19·72° at 68·5°; 18·76° at 85°; 18·10° at 100°; 17·34° at 120°.

a_{4358} 37·14° at 22°; 35·62° at 37·5°; 34·66° at 50°; 33·34° at 67·5°; 32·16° at 85°*; 30·86° at 100°; 29·42° at 119°.

* While cooling.

TABLE III.

Ethers of d-Benzylmethylcarbinol.

Methyl ether.

$t°$.	$D_4^{t°}$.				$[\alpha]_\lambda^t$.		
		λ 6438.	λ 5461.	λ 5086.	λ 4800.	λ 4678.	λ 4358.
20°	0·9354	4·58°	6·35°	7·63°	8·75°	9·28°	10·80°
40	0·9187	4·20	5·53	6·71	7·75	8·23	9·27
60	0·9013	3·73	4·73	5·75	6·68	7·12	7·73
80	0·8842	3·26	4·07	4·77	5·61	6·06	6·47
100	0·8670	2·68	3·40	3·99	4·57	4·94	5·38
120	0·8490	2·19	2·71	3·23	3·60	3·98	4·35

Ethyl ether.

$t°$.	$D_4^{t°}$.				$[\alpha]_\lambda^t$.		
		λ 6438.	λ 5461.	λ 5086.	λ 4800.	λ 4678.	λ 4358.
20°	0·9203	17·78°	25·75°	30·27°	35·14°	37·33°	44·34°
40	0·9035	17·16	24·68	29·16	33·91	36·15	42·69
60	0·8865	16·39	23·40	27·99	32·54	34·82	40·94
80	0·8697	15·62	22·47	26·79	31·18	33·46	39·13
100	0·8527	14·83	21·46	25·69	29·74	32·08	37·36
120	0·8358	14·19	20·43	24·67	28·40	30·70	35·54
140	0·8189	13·77	19·54	23·63	27·06	29·25	33·67

n-Propyl ether.

$t°$.	$D_4^{t°}$.				$[\alpha]_\lambda^t$.		
		λ 6438.	λ 5461.	λ 5086.	λ 4800.	λ 4678.	λ 4358.
20°	0·9132	17·78°	25·93°	30·66°	34·99°	37·26°	44·63°
40	0·8968	17·31	25·09	29·75	33·98	35·97	43·00
60	0·8804	16·79	23·90	28·39	32·62	34·42	41·02
80	0·8639	16·15	22·78	27·08	30·97	32·80	39·21
100	0·8474	15·38	21·83	26·10	29·79	31·49	37·58
120	0·8308	14·83	21·15	25·32	29·10	30·86	36·59

n-Butyl ether.

$t°$.	$D_4^{t°}$.				$[\alpha]_\lambda^t$.		
		λ 6438.	λ 5461.	λ 5086.	λ 4800.	λ 4678.	λ 4358.
20°	0·9032	19·42°	27·90°	33·09°	37·93°	39·90°	48·22°
40	0·8872	19·03	26·99	32·03	36·75	38·67	46·38
60	0·8713	18·50	26·01	30·82	35·41	37·38	44·49
80	0·8556	17·80	24·95	29·70	34·13	36·04	42·71
100	0·8398	17·24	23·95	28·70	32·91	34·77	41·31
120	0·8239	16·67	23·11	27·84	31·85	33·62	40·05
140	0·8080	16·43	22·43	26·99	30·94	32·58	39·05

TABLE III.—(continued).

Ethers of d-Benzylmethylcarbinol.

n-Amyl ether.

$t°$	$D_4^{t°}$	$[\alpha]_\lambda^{t°}$		
		λ 5893.	λ 5461.	λ 4358.
20°	0·8938	22·75°	26·85°	46·48°
40	0·8789	22·08	25·99	45·03
60	0·8631	21·43	25·23	43·51
80	0·8476	20·66	24·46	41·88
100	0·8322	19·71	23·48	39·94
120	0·8166	18·66	22·31	38·04
140	0·8011	17·73	21·17	36·20

n-Hexyl ether.

$t°$	$D_4^{t°}$	$[\alpha]_\lambda^{t°}$		
		λ 5893.	λ 5461.	λ 4358.
20°	0·8917	22·83°	27·03°	46·40°
40	0·8765	22·18	26·01	44·77
60	0·8611	21·53	25·11	43·21
80	0·8460	20·83	24·18	41·79
100	0·8307	20·27	23·52	40·68
120	0·8155	19·91	23·00	39·82
140	0·8005	19·79	22·81	39·22

n-Heptyl ether.

$t°$	$D_4^{t°}$	$[\alpha]_\lambda^{t°}$					
		6438.	5461.	5086.	4800.	4678.	4358.
20°	0·8862	18·10°	25·84°	30·43°	34·92°	36·90°	44·26°
40	0·8719	17·55	24·99	29·43	33·75	35·82	42·67
60	0·8572	16·85	24·03	28·34	32·59	34·60	41·08
80	0·8430	16·43	23·20	27·45	31·61	33·50	39·53
100	0·8287	15·93	22·49	26·67	30·60	32·48	38·32
120	0·8142	15·52	21·86	25·84	29·57	31·49	37·35
140	0·8005	15·16	21·28	24·98	28·61	30·35	36·38

n-Octyl ether.

$t°$	$D_4^{t°}$	$[\alpha]_\lambda^{t°}$					
		6438.	5461.	5086.	4800.	4678.	4358.
20°	0·8850	17·29°	25·14°	29·43°	33·67°	35·76°	42·56°
40	0·8707	16·73	24·29	28·61	32·91	34·85	41·49
60	0·8565	16·23	23·42	27·59	31·94	33·71	40·24
80	0·8422	15·63	22·66	26·62	30·92	32·56	38·95
100	0·8279	15·19	21·91	25·77	29·84	31·46	37·52
120	0·8135	14·80	21·16	24·98	28·89	30·54	36·21
140	0·7992	14·44	20·70	24·15	27·99	29·63	35·14

n-Nonyl ether.

$t°$	$D_4^{t°}$	$[\alpha]_\lambda^{t°}$		
		λ 5893.	λ 5461.	λ 4358.
20°	0·8835	20·78°	24·85°	42·08°
40	0·8712	20·20	24·01	40·80
60	0·8569	19·48	23·29	39·56
80	0·8427	18·91	22·50	38·40
100	0·8285	18·59	21·82	37·26
120	0·8140	18·26	21·35	36·16
140	0·7997	18·01	20·76	35·26

TABLE IV.

Determinations of Rotatory Power in (approx.) 5 per cent. Ethyl Alcohol Solution.

Length of observation tube 20 cm.　T = 17°.

Ether.	Grams of substance in 100 c.c. of solution.	Observed rotation.			$[\alpha]_\lambda^{t°}$.		
		λ 5893.	λ 5461.	λ 4358.	λ 5893.	λ 5461.	λ 4358.
Methyl	5·00	0·28°	0·49°	0·73°	2·8°	4·9°	7·3°
Ethyl	4·95	1·95	2·42	4·07	19·7	24·4	41·1
Propyl	5·01	2·11	2·41	4·14	21·1	24·0	41·3
Butyl	5·00	2·53	3·06	4·94	25·3	30·6	49·4
Amyl	4·91	2·52	3·06	5·02	25·6	31·1	51·1
Hexyl	5·04	2·57	3·09	5·06	25·5	30·7	50·3
Heptyl	5·07	2·51	3·02	5·00	24·8	29·8	49·3
Octyl	4·95	2·40	2·95	4·85	24·2	29·8	49·0
Nonyl	5·04	2·46	2·99	4·90	24·4	29·7	48·6

TABLE V.

Determinations of Rotatory Power in (approx.) 5 per cent. Carbon Disulphide Solution.

Length of observation tube 20 cm.　T = 17°.

Ether.	Grams of substance in 100 c.c. of solution.	Observed rotation.			$[\alpha]_\lambda^{t°}$.		
		λ 5893.	λ 5461.	λ 4358.	λ 5893.	λ 5461.	λ 4358.
Methyl	5·00	3·62°	3·95°	8·13°	36·2°	39·5°	81·3°
Ethyl	5·01	4·45	5·15	9·45	44·4	51·4	94·3
Propyl	5·00	4·28	5·21	9·32	42·8	52·1	93·2
Butyl	4·98	4·26	5·28	9·49	42·7	53·0	95·2
Amyl	5·01	4·16	4·83	8·92	41·5	48·1	89·1
Hexyl	4·99	4·11	4·98	9·01	41·2	49·9	90·3
Heptyl	4·87	3·71	4·60	8·00	38·1	47·2	82·1
Octyl	5·05	3·82	4·60	8·26	37·9	45·6	81·9
Nonyl	4·96	3·72	4·43	8·00	37·5	44·6	80·6

IV.—*Investigations on the Dependence of Rotatory Power on Chemical Constitution. Part XVI. The Di-d-β-octyl Esters of the Saturated Dicarboxylic Acids.*

By Leslie Hall.

Among the results which emerge from this series of investigations are the interesting differences which have been observed in the optical rotatory and rotatory dispersive powers of aliphatic secondary alcohols and aliphatic ethers derived from them, on the one hand, and of aliphatic esters derived from the same alcohols, on the other.

Considering the rotatory powers first, it has been shown that those of the esters are, in general, much more susceptible to the influences of temperature, dissolution, and concentration than are those of the alcohols from which they are derived and of the ethers which may be derived from the same alcohols. Compare, for example, the differences in the temperature–rotation curves of *d-sec.*-octyl alcohol and of *d-sec.*-octyl acetate (Part I, T., 1911, **99**, 50; Part V, T., 1914, **105**, 837) and in the alterations in rotatory power which they respectively exhibit in certain solvents, notably carbon disulphide.

A legitimate deduction which may be drawn from a consideration of these and other facts is that the differences in behaviour shown by the esters may be due to some inherent property of the carboxyl group, and in order to obtain further evidence bearing on this point, a series of optically active esters derived from *d-sec.*-octyl alcohol and some saturated aliphatic normal dicarboxylic acids has been prepared and their optical behaviour investigated.

A series of optically active esters of aliphatic dibasic acids has been previously described in the literature by Walden (*J. Russ. Phys. Chem. Soc.*, 1898, **30**, 767), who used the fermentation amyl alcohol; this, however, was not optically pure (compare Marckwald and McKenzie, *Ber.*, 1901, **34**, 485), so that any deductions derived from a consideration of his results are unreliable.

Moreover, in this and other earlier work, the optical rotatory powers were determined for light of one wave-length only, and the measurements made only at the temperature of the laboratory.

The results of the polarimetric determinations tabulated on pp. 41 and 42, show that the esters herein described exhibit complex rotatory dispersion under all conditions employed, namely, in the homogeneous condition at temperatures from 20° to 130°,

and in solution in carbon disulphide and in ethyl alcohol at the ordinary temperature.

Not more than one ester, however, d-β-octyl succinate, was observed to exhibit anomalous rotatory dispersion in the region

FIG. 1.

Number of methylene groups in acid (n).
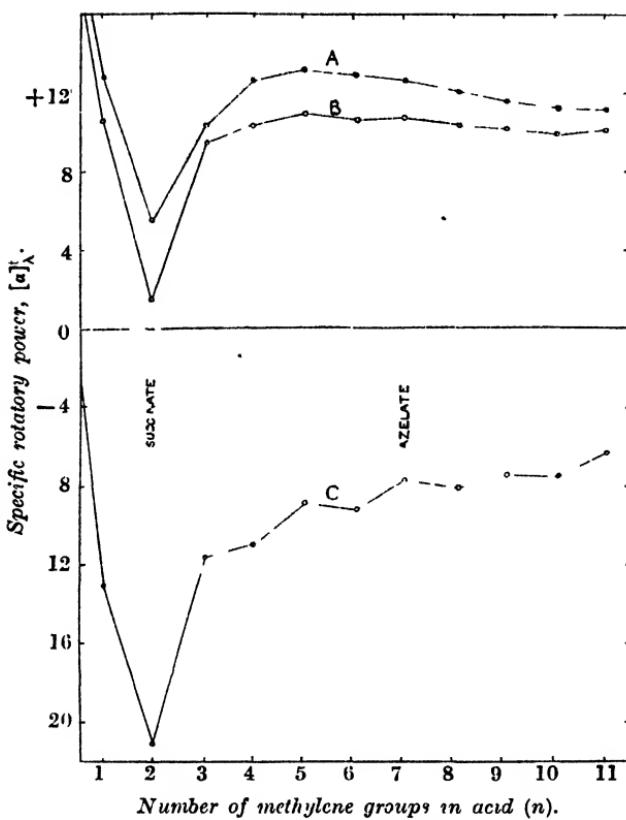
The d-β-octyl esters of the dibasic acids $(CH_2)_n(CO·OH)_2$.

    A. $[a]_{461}^{10°}$ *in the homogeneous state.*

    B. $[a]_{461}$ *in 5% solution in ethyl alcohol.*

    C. $[a]_{5893}$ „ „ „ „ *carbon disulphide.*

of the spectrum studied, and then only in 5 per cent. solution in ethyl alcohol at 18°.

An examination of the curves (Fig. 1) obtained by plotting the specific rotatory powers of the various esters against the number of methylene groups in the respective acids, shows:

(1) The oxalic ester possesses a particularly large optical rotation: a similar result was observed by Hilditch in the case of

l-menthyl oxalate (T., 1909, **95**, 1581), and the explanation of this given by Hilditch, namely, that the contiguity of the two carboxyl groups in the oxalic acid residue is the cause of the exaltation in its esters, appears to be satisfactory.

(2) The succinic ester has a very small rotation. Now it has been observed in these series of investigations that chains of five, ten, fifteen, etc., atoms are often associated with peculiarities in optical behaviour. If the formula of this ester be written as follows,

$$CH_3 \cdot CH(C_6H_{13}) \cdot O \cdot CO \cdot CH_2$$
$$H_2C \cdot CO \cdot O \cdot CH(C_6H_{13}) \cdot CH_3$$
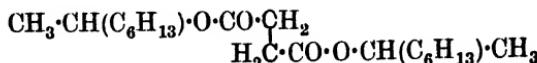
it is apparent that there is the possibility of two chains containing five atoms or of two containing ten atoms, each influencing abnormally the magnitude of the optical rotatory power.

(3) The rotation values are alternately high and low as the series is ascended. This may be due to the alternate members of the oxalic acid series possessing a *cis*- or *trans*-configuration respectively. An analogous alternation is also known in a number of other physical properties of this series, for example, the melting points, solubility in water, solubility of the calcium salts, melting points of the methyl esters.

This view of the alternate *cis*- and *trans*-structure of this series has received support from the recent work of Irvine and Steele (T., 1915, **107**, 1221) and Price and Brazier (*ibid.*, **107**, 1719).

The latter authors, as a result of their work on the formation of additive compounds of complex metallic ammines with these dicarboxylic acids, make the tentative suggestion that oxalic, succinic, and adipic acids possess a *trans*-configuration, whilst malonic and glutaric acids possess a *cis*-configuration. Such considerations on stereochemical grounds render untenable any assumption of the configuration of the succinic ester as containing chains of fifteen or twenty atoms, but it is suggested that the assumption of a configuration made up of two spirals agrees with the hypothesis advanced to account for the low rotation of the ester.

Experimental.

The active β-octanol required for the preparation of the esters was made by the method described by Kenyon (T., 1922, **121**, 2540).

Of the dibasic acids employed, suberic and sebacic acids were obtained from Kahlbaum, whilst the others were prepared by the following methods :

Glutaric acid from trimethylene cyanide (Auger, *Ann. Chim. Phys.*, 1901, [vi], **22**, 357).

Adipic acid by the oxidation of *cyclo*hexanol with nitric acid (Bouveault and Locquin, *Bull. Soc. chim.*, 1908, [iv], **3**, 438).

Pimelic acid from trimethylene bromide and malonic ester (Blaise and Koehler, *ibid.*, 1909, [iv], **5**, 687).

Azelaic acid from castor oil (Maquenne, *ibid.*, 1899, [iii], **21**, 1061).

n-Nonane-, *n*-decane-, and *n*-undecane-dicarboxylic acids from undecenoic acid. The undecenoic acid was converted into ω-bromo-undecoic acid by the method of Walker and Lumsden (T., 1901, **79**, 1191). After a number of trials, it was ascertained that good yields of ω-bromoundecoic acid can only be obtained by this method if the undecenoic acid is carefully purified beforehand by rapid distillation under diminished pressure.

The acid chlorides were prepared by mixing the pure dry acids with thionyl chloride (H. Meyer, *Monatsh.*, 1901, **22**, 421); the acid chlorides of the higher members of the series were not distilled owing to their instability at the high temperatures necessary.

d-β-*Octyl oxalate* was prepared by three methods : (i) by heating anhydrous oxalic acid with four times its weight of *d*-β-octyl alcohol at 150° for two hours followed by fractional distillation under diminished pressure; (ii) by heating ethyl oxalate with *d*-β-octyl alcohol (2 mols.) (*a*) at 175—180° for about ten hours in an uncorked flask, or (*b*) at 195—205° for about ten hours in a small aluminium autoclave, followed in each case by fractional distillation; (iii) by using methyl oxalate and working up the product as under (ii).

The following products were isolated as colourless liquids : *d*-β-octyl oxalate, b. p. 198—199°/11 mm., very faint odour; *d*-β-octyl ethyl oxalate, b. p. 138—140°/20 mm., fruity odour; and *d*-β-octyl methyl oxalate, b. p. 130—132°/20 mm., fruity odour.

d-β-*Octyl malonate* was prepared by method (ii) as described under the oxalate, using ethyl malonate, and also by method (i) with the modification that the mixture of malonic acid (7 grams) and *d*-β-octyl alcohol was treated with dry hydrogen chloride until 1 gram had been absorbed before it was heated at 100° for three hours. The reaction product was washed with sodium carbonate solution before distillation.

The following substances were isolated as colourless liquids : *d*-β-octyl malonate, b. p. 158—160°/19 mm., fruity odour; and *d*-β-octyl ethyl malonate, b. p. 198—200°/19 mm., fruity odour.

d-β-Octyl ethyl malonate was prepared also by the interaction of *d*-β-octyl alcohol and the acid chloride of ethyl hydrogen malonate.

TABLE I.

Refractive Indices (n_λ) of the Esters.

Ester.	Temp.	λ 6438	λ 5896	λ 5461	λ 5086	λ 4800	λ 4678	λ 4358
d-β-Octyl								
oxalate	26°	1 4309	1 4329	1 4347	1 4366	1 4385	1 4395	1 4426
malonate	26 2	1 4326	1 4345	1 4365	1 4384	1 4404	1 4412	1 4443
succinate	25 8	1 4349	1 4367	1 4386	1 4407	1 4427	1 4435	1 4463
glutarate	25 8	1 4365	1 4384	1 4401	1 4423	1 4441	1 4452	1 4480
adipate	25		1 4402	1 4421				1 4497
pimelate	25 8	1 4392	1 4409	1 4429	1 4450	1 4470	1 4479	1 4509
suberate	25 7	1 4400	1 4419	1 4439	1 4459	1 4476	1 4496	1 4516
azelate	25	1 4412	1 4432	1 4450	1 4470	1 4490	1 4501	1 4532
sebacate	25 8	1 4421	1 4441	1 4460	1 4479	1 4499	1 4511	1 4538
n-nonane-α-di-carboxylate	25		1 4448	1 4466				1 4545
n-decane-αα-di-carboxylate	25 8	1 4453	1 4463	1 4485	1 4501	1 4521	1 4530	1 4560
n-undecane-α-dicarboxylate	25		1 4456	1 4475				1 4553
d β Octyl								
m-thyl oxalate	25		1 4261	1 4280				1 4357
ethyl oxalate	26	1 4234	1 4253	1 4277	1 4304	1 4311	1 4320	1 4348
ethyl malonate	26	1 4249	1 4269	1 4286	1 4303	1 4323	1 4333	1 4361
l-β-Octyl								
methyl succinate	25		1 4305	1 4323				1 4399
d-β Octyl								
ethyl succinate	25 6	1 4289	1 4308	1 4326	1 4346	1 4364	1 4374	1 4402

TABLE II.

Molecular Refractive Powers $[R_L]^t_{5896}$ of the Esters.

Ester.	D_4^t	n^t_{5896}	Observed $\dfrac{n^2-1}{n^2+2} \cdot \dfrac{M}{D_4^t}$	Difference from calc. value.
d-β-Octyl				
oxalate	0 9147	1 4329	89 27	+ 0 64
malonate	0 9150	1 4345	93 51	+ 0 26
succinate	0 9127	1 4367	98 18	+ 0 31
glutarate	0 9115	1 4384	102 69	+ 0 20
adipate	0 9094	1 4402	107 36	+ 0 26
pimelate	0 9072	1 4409	111 75	+ 0 03
suberate	0 9038	1 4419	116 59	+ 0 25
azelate	0 9018	1 4432	121 27	+ 0 31
sebacate	0 9000	1 4441	125 87	+ 0 29
n-nonane-α-di-carboxylate	0 9091	1 4448	130 31	+ 0 12
n-decane-αα-di-carboxylate	0 8990	1 4463	134 36	− 0 25
n-undecane-α-dicarboxylate	0 8938	1 4456	139 64	+ 0 21
d β Octyl				
m-thyl oxalate	0 9790	1 4261	56 60	+ 0 30
ethyl oxalate	0 9574	1 4253	61 50	+ 0 58
ethyl malonate	0 9594	1 4269	65 35	− 0 19
l-β-Octyl				
methyl succinate	0 9629	1 4305	65 60	+ 0 06
d-β Octyl				
ethyl succinate	0 9548	1 4308	69 96	− 0 20

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TABLE III.

Observed Densities and Rotatory Powers of the Esters.

Rotations are here given as for a 1-dcm. tube.

</div>

d-β-Octyl oxalate.

$D_4^{t^{\circ}}$ 0·9147 at 26°; 0·9040 at 40·5°; 0·8863 at 63°; 0·8720 at 80·5°; 0·8563 at 100°.

α_{5893} 20·94° at 18·8°; 20·48° at 27·3°; 19·98° at 41°; 17·20° at 82°; 16·62° at 97°; 15·94° at 124°.

α_{5461} 24·52° at 18·8°; 23·78° at 27·5°; 21·64° at 49°; 19·84° at 80°; 18·86° at 97°; 17·98° at 130°.

α_{4358} 37·62° at 19·4°; 36·76° at 27·5°; 33·26° at 49°; 31·46° at 80°; 29·80° at 98°; 28·20° at 130°.

d-β-Octyl malonate.

$D_4^{t^{\circ}}$ 0·9189 at 21·2°; 0·9005 at 45·5°; 0·8837 at 65°; 0·8706 at 80°; 0·8574 at 99°; 0·8395 at 122·5°.

α_{6438} 8·48° at 19·2°; 7·32° at 40°; 5·74° at 77°; 5·04° at 102°; 4·72° at 122°; 4·12° at 158°.

α_{5461} 11·76° at 19·2°; 10·24° at 41°; 8·16° at 76°; 7·04° at 100°; 6·34° at 122°; 5·72° at 158°.

α_{5086} 13·60° at 19·2°; 11·60° at 40°; 9·08° at 77°; 7·70° at 102°; 7·08° at 122°; 6 28° at 157°.

α_{4800} 15·18° at 19·2°; 12·86° at 40°; 10·02° at 77°; 8·56° at 102°; 7·86° at 122°; 6·72° at 157°.

α_{4678} 15·64° at 19·2°; 13·52° at 40°; 10·70° at 77°; 9·14° at 102°; 8·28° at 122°; 7·26° at 157°.

α_{4358} 17·82° at 19·2°; 15·02° at 41°; 11·86° at 76°; 10·12° at 100°; 9·00° at 122°; 7·72° at 158°.

d-β-Octyl succinate.

D_4^{t} 0·9175 at 19·7°; 0·8982 at 44·5°; 0·8853 at 60·3°; 0·8700 at 81·2°; 0·8511 at 107°; 0·8405 at 120·5°   0·8222 at 142°; 0·8072 at 162·5°.

α_{6438} 3·76° at 19·2°; 3 36° at 57°; 3·14° at 81°   3·10° at 128°   3·14° at 144°.

α_{5461} 5·04° at 19·2°; 4 64° at 56°; 4·14° at 82°   4·26° at 126°   4·06° at 144°.

α_{5086} 5·48° at 19·2°; 4·86° at 57°; 4·50° nt 81°   4·64° at 128°   4·56° at 144°.

α_{4800} 6 12° at 19·2°; 5·28° at 59°; 4·96° at 81°   4·94° at 128°   4·88° at 144°.

α_{4678} 6·46° at 19·2°; 5·60° at 59°; 5·44° at 81°   5 30° at 128°   5·12° at 144°.

α_{4358} 7·02° at 19·2°; 6·02° at 56°; 5·72° at 81°   5·56° at 126°   5·52° at 144°.

d-β-Octyl glutarate.

$D_4^{t^{\circ}}$ 0·9204 at 15°; 0·9040 at 35·5°; 0·8921 at 50·5°; 0·8688 at 82·5°; 0·8543 at 100°; 0·8358 at 124°; 0·8213 at 143°; 0·8035 at 164°.

α_{6438} 6·70° at 17°; 5·92° at 37·6°; 4·70° at 69°; 4·14° at 98°; 3·80° at 125°; 3·52° at 147°.

α_{5461} 9·78° at 17°; 8·32° at 37·2°; 6·84° at 68°; 5·78° at 99°; 5·24° at 122°; 4·74° at 148°.

α_{5086} 10·88° at 17°; 9·52° at 37·6°; 7·48° at 69°; 6·52° at 98°; 5·62° at 125°; 5·42° at 147°.

α_{4800} 12·12° at 17°; 10·50° at 37·6°; 8·22° at 69°; 7·18° at 98°; 6·50° at 125°; 6·08° at 147°.

α_{4678} 12·60° at 17°; 11·02° at 37·6°; 8·70° at 69°; 7·56° at 98°; 6·98° at 125°; 6·38° at 147°.

α_{4358} 14·88° at 17°; 12·38° at 37·2°; 10·04° at 68°; 8·68° at 99°; 8·00° at 122°; 7·12° at 148°.

d-β-Octyl adipate.

$D_4^{t^o}$ 0·9072 at 28°; 0·8933 at 46·25°; 0·8774 at 68°; 0·8602 at 90·5°; 0·8371 at 124°.

α_{5893} 10·20° at 19·8°; 9·90° at 28·5°; 8·50° at 60°; 7·36° at 85°; 6·74° at 108°; 6·02° at 121°.

α_{5461} 11·58° at 19·8°; 11·14° at 28·5°; 9 34° at 59°; 8·42° at 84°; 7·24° at 108°; 6·86° at 122°.

α_{4358} 18·20° at 19·8°; 17·32° at 28·5°; 15·10° at 59°; 13·28° at 84°; 11·46° at 108°; 10·86° at 122'.

d-β-Octyl pimelate.

$D_4^{t^o}$ 0·9111 at 21°; 0·8948 at 41·5°; 0·8792 at 63·5°; 0·8666 at 80·5°; 0·8519 at 99·5°; 0·8347 at 123°; 0·8181 at 143°; 0·8058 at 161°.

σ_{6138} 8·68° at 19·5°; 7·76° at 37·2°; 6·32° at 73·5°; 5·78° at 97°; 5·10° at 127°; 4·68° at 145°.

α_{5461} 12·02° at 19·5°; 10·38° at 39°; 8·32° at 73·5°; 7·58° at 99·2°; 6·78° at 126°; 6·20° at 145°.

α_{5086} 14·00° at 19·5°; 12·40° at 38°; 9·70° at 76°; 8·70° at 97°; 8·08° at 127°; 7·44° at 145°.

α_{4800} 15 68° at 19·5°; 13·78° at 38°; 10·62° at 74°; 9·92° at 97°; 9·02° at 127°; 8·02° at 145°.

α_{4678} 16 60° at 19·5°; 14·22° at 39°; 11·06° at 73°; 10·58° at 97°; 9·52° at 127°; 9·00° at 145°.

α_{4358} 18·80° at 19·5°; 16·02° at 40°; 12·86° at 73°; 11·54° at 99·2°; 10·60° at 126°; 10·04° at 145°.

d-β-Octyl suberate.

D_4^{t} 0 9084 at 20°; 0·8925 at 41°; 0·8788 at 60·7°; 0·8640 at 80·5°; 0·8492 at 100°; 0·8285 at 128°.

α_{5893} 9·80° at 22·6°; 8·92° at 149°; 7 56° at 76°; 6·56° at 92°; 6·06° at 102°; 5·56° at 127°.

α_{5461} 11·56° at 22·6°; 10·04° at 48°; 8·42° at 75°; 7·76° at 92°; 7·56° at 102°; 7·14° at 127°.

α_{4358} 17·58° at 22·6°; 15·50° at 48°; 14 26° at 75°; 12·92° at 92°; 12·08° at 102°; 10·72° at 127°.

d-β-Octyl azelate.

$D_4^{t^o}$ 0·9053 at 20°; 0·8908 at 40·8°; 0·8768 at 60·7°; 0·8640 at 80°; 0·8486 at 100°; 0·8324 at 121°; 0·8191 at 142°; 0·8037 at 163°; 0·7874 at 185°; 0·7695 at 210°.

α_{6438} 8·18° at 19·4°; 6·94° at 51·7°; 6·48° at 67°; 5·98° at 95°; 5·30° at 107°; 4·88° at 129°.

α_{5461} 11·66° at 19·4°; 9·94° at 45°; 8·98° at 67°; 8·26° at 80°; 7·80° at 95°; 7·62° at 107°; 7·04° at 129°.

α_{5086} 13·28° at 19·4°; 11·52° at 51·7°; 10·36° at 67°; 9·98° at 80°; 8·94° at 95°; 8·58° at 107°; 7·52° at 129°.

α_{4800} 14·76° at 19·4°; 12·62° at 51·2°; 11·50° at 67°; 10·90° at 80°; 9·94° at 95°; 9·38° at 107°; 8·40° at 129°.

α_{4678} 15·40° at 19·4°; 12·92° at 51·7°; 11·98° at 67°; 11·24° at 80°; 10·24° at 95°; 9·82° at 107°; 8·68° at 129°.

α_{4358} 17·96° at 19·4°; 15·12° at 47°; 13·56° at 67°; 13·08° at 80°; 11·90° at 95°; 11·68° at 107°; 10·52° at 129°.

d-β-Octyl sebacate.

$D_c^{t'}$ 0·0935 at 20·6°; 0·8898 at 39·8°; 0·8730 at 79°; 0·8474 at 99·8°; 0·8305 at 123°; 0·8137 at 146°; 0·8019 at 163°.

α_{6438} 7·98° at 18·8°; 6·38° at 48·8°; 5·46° at 78°; 4·88° at 99°; 4·64° at 128°; 4·12° at 152°.

α_{5461} 10·86° at 18·8°; 9·34° at 51°; 7·56° at 77·5°; 6·50° at 106°; 5·94° at 130°; 5·26° at 155°.

α_{5086} 12·84° at 18·8°; 10·58° at 48·8°; 8·88° at 78°; 7·84° at 100°; 7·04° at 128°; 6·42° at 152°.

α_{4800} 14·36° at 18·8°; 11·64° at 48·8°; 9·62° at 79°; 8·80° at 101°; 7·56° at 128°.

α_{4678} 15·28° at 18·8°; 12·30° at 48·8°; 9·88° at 80°; 8·88° at 102°; 8·42° at 128°.

α_{4358} 17·16° at 18·8°; 13·72° at 51°; 12·00° at 77·5°; 9·94° at 106°; 9·10° at 130·5°; 8·70° at 155°.

d-β-Octyl n-nonane-$\alpha\iota$-dicarboxylate.

$D_c^{t'}$ 0·8991 at 25°; 0·8839 at 46°; 0·8744 at 61·5°; 0·8612 at 79°; 0·8463 at 98°.

α_{5893} 9·36° at 20°; 8·42° at 37°; 8·04° at 48·2°; 7·40° at 65°; 6·98° at 81°; 5·96° at 103°; 5·20° at 120°; 4·64° at 132°.

α_{5461} 10·64° at 20°; 9·50° at 37°; 8·84° at 47°; 8·26° at 65°; 7·62° at 81°; 6·70° at 97°; 6·02° at 118°; 5·34° at 132°.

α_{4358} 16·58° at 20°; 14·48° at 37°; 13·58° at 47°; 12·68° at 65°; 11·58° at 81°; 10·58° at 97°; 8·90° at 120°; 8·22° at 132°.

d-β-Octyl n-decane-$\alpha\kappa$-dicarboxylate.

$D_c^{t'}$ 0·8960 at 30°; 0·8810 at 50·5°; 0·8678 at 69°; 0·8543 at 89°; 0·8266 at 124°; 0·8110 at 142°.

α_{5893} 9·38° at 20·2°; 8·24° at 35°; 7·60° at 54°; 6·94° at 71°; 6·26° at 85°; 5·92° at 99°; 5·60° at 120°.

α_{5461} 10·22° at 20·2°; 9·68° at 33°; 8·40° at 54°; 7·96° at 71°; 7·24° at 85°; 6·70° at 99°; 6·16° at 120°; 5·90° at 133°.

α_{4358} 15·38° at 20·2°; 14·20° at 33°; 12·80° at 54°; 12·00° at 71°; 11·32° at 85°; 10·72° at 99°; 9·70° at 120°.

d-β-Octyl n-undecane-$\alpha\lambda$-dicarboxylate.

$D_4^{t'}$ 0·8894 at 31°; 0·8746 at 51°; 0·8606 at 70°; 0·8468 at 90°; 0·8231 at 120°; 0·8021 at 142°.

α_{5893} 8·28° at 21°; 7·94° at 32°; 7·52° at 49°; 7·32° at 71°; 6·86° at 95°; 6·66° at 110°; 6·26° at 126°.

α_{5461} 9·96° at 21°; 9·44° at 32°; 8·90° at 50°; 8·16° at 71°; 7·58° at 95°; 7·00° at 110°; 6·68° at 126°.

α_{4358} 15·66° at 21°; 14·46° at 32°; 13·50° at 50°; 12·18° at 71°; 11·06° at 95°; 10·14° at 110°; 9·66° at 126°.

d-β-Octyl methyl oxalate.

$D_c^{t'}$ 0·9745 at 30°; 0·8563 at 50°; 0·9380 at 70·5°; 0·9183 at 90°; 0·8894 at 119°; 0·8636 at 140°.

α_{5893} 14·04° at 19°; 13·08° at 34°; 11·90° at 64°; 11·14° at 90°; 10·24° at 112°; 9·56° at 126°.

α_{5461} 16·54° at 19°; 15·04° at 35°; 14·00° at 60°; 12·38° at 90°; 11·44° at 112°; 10·74° at 126°.

α_{4358} 25·72° at 19°; 24·00° at 34°; 22·10° at 59°; 19·62° at 90°; 18·68° at 112°; 17·42° at 126°.

d-β-Octyl ethyl oxalate.

$D_4^{t^\circ}$ 0·9574 at 26·5°; 0·9428 at 43°; 0·9251 at 62·5°; 0·9067 at 82°.

a_{5893} 13·20° at 24°; 11·88° at 53°; 11·58° at 73°; 11·08° at 96°; 10·84° at 116°.

a_{5461} 15·40° at 24°; 13·60° at 53°; 12·62° at 73°; 12·14° at 96°; 11·60° at 116°.

a_{4358} 23·68° at 24°; 21·24° at 53°; 19·46° at 73°; 18·08° at 96°; 16·98° at 116°.

d β-Octyl ethyl malonate.

$D_4^{t^\circ}$ 0·9519 at 28°; 0·9328 at 49°; 0·9175 at 68°; 0·8867 at 100·5°.

a_{5893} 8·82° at 21·5°; 7·86° at 35°; 7·02° at 54°; 6·24° at 75°; 5·90° at 92°; 5·18° at 108°.

a_{5461} 10·38° at 21·5°; 9·16° at 35°; 7·92° at 55°; 7·18° at 75°; 6·04° at 93°; 5·78° at 111°.

a_{4358} 16·52° at 21·5°; 14·94° at 35°; 13·02° at 55°; 11·84° at 75°; 10·64° at 93°; 8·86° at 110°.

l-β-Octyl methyl succinate.

$D_4^{t^\circ}$ 0·9627 at 25°; 0·9508 at 39·5°; 0·9330 at 60°; 0·9164 at 80°; 0·8989 at 100°; 0·8782 at 123°.

a_{5893} — 3·42° at 19·5°; — 3 32° at 36°; — 3·12° at 58°; — 2·88° at 84°; — 2·58° at 106°; — 2·38° at 126°.

a_{5461} — 3·84° at 19 5°; — 3·76° at 34°; — 3·46° at 58°; — 3·14° at 80°; — 2 84° at 106°; — 2·56° at 125°.

a_{4358} — 5·64° at 19·5°; — 5·46° at 35°; — 5·04° at 58°; — 4·64° at 86°; — 4 34° at 106°; — 4·08° at 125°.

d-β-Octyl ethyl succinate.

$D_4^{t^\circ}$ 0·9614 at 17·4°; 0 9434 at 39·5°; 0·9223 at 63·3°; 0·9090 at 79°; 0·8904 at 102°; 0·8746 at 123°.

a_{6438} 2·40° at 18·2°; 2·24ᶜ at 30·2°; 2·16° at 52°; 2 06° at 79°; 1·94 at 107°; 1·64° at 124°.

a_{5431} 3 58° at 18·2°; 3·36° at 30·5°; 3 22° at 51°; 3·06° at 80°; 2·80° at 107°; 2·76ᵘ at 120°.

a_{5086} 3·84° at 18 2°; 3·68° at 30·2°; 3·46° at 52°; 3 20° at 78°; 2·92° at 107°; 2 92° at 121°.

a_{4800} 4·24° at 18·2°; 4·08° at 30·2°; 3·72° at 52°; 3·50° at 78°; 3·40° at 107°; 3·22° at 121°.

a_{4678} 4·42° at 18 2 ; 4·28° at 30 2°; 3·92° at 52°; 3·74° at 78°; 3·68° at 107°.

a_{4358} 5·22° at 18·2°; 4·90° at 30 5°; 4·58° at 51°; 4·28° at 80°; 4·08° at 107°.

d-β-*Octyl succinate* was prepared by method (ii) using ethyl succinate, by method (iii) using methyl succinate, and also by the interaction of succinyl chloride and d-β-octyl alcohol.

The products obtained were : d-β-octyl succinate, b. p. 208—211°/16 mm., very faint odour; d-β-octyl ethyl succinate, b. p. 160—162°/16 mm., fruity odour; and l-β-octyl methyl succinate, b. p. 163—164°/15 mm., fruity odour.

The remaining esters were obtained by the interaction of d-β-octyl alcohol and the required acid chloride as colourless, somewhat viscous, almost odourless liquids and possessed the following boiling points : glutarate, b. p. 175—177°/3 mm.; adipate, b. p. 175°/2 mm.; pimelate, b. p. 188—190°/3 mm.; suberate, b. p. 202—204°/3 mm.; azelate, b. p. 208—210°/2 mm.; sebacate, b. p. 240—242°/7 mm.; n-nonanedicarboxylate, b. p. 205—207°/1 mm.; n-decanedicarb-

TABLE IV.

Densities and Rotatory Powers of the Esters.

d-β-Octyl oxalate.

t°.	D_4^t	[α]5893°	[α]5461°	[α]4358°
20°	0·9198	22·72°	26·57°	40·66°
40	0·9043	21·56	24·93	38·77
60	0·8884	20·60	23·72	37·15
80	0·8725	19·86	22·83	35·96
100	0·8561	19·32	22·26	34·92
120	0·8397	18·98	21·77	34·00

d-β-Octyl malonate.

t°.	D_4^t	[α]6438°	[α]5461°	[α]5086°	[α]4800°	[α]4678°	[α]4358°
20°	0·9198	9·19°	12·83°	14·79°	16·37°	17·07°	19·37°
40	0·9038	8·08	11·33	12·88	14·23	14·89	16·62
60	0·8883	7·09	10·18	11·44	12·68	13·40	14·60
80	0·8729	6·42	9·17	10·24	11·39	12·08	13·11
100	0·8574	5·95	8·40	9·33	10·29	10·98	11·90
120	0·8424	5·51	7·76	8·62	9·43	10·09	10·92

d-β-Octyl succinate.

t°.	D_4^t	[α]4638°	[α]5461°	[α]5086°	[α]4800°	[α]4678°	[α]4358°
20°	0·9171	4·08°	5·54°	6·00°	6·65°	7·02°	7·63°
40	0·9017	3·93	5·32	5·77	6·39	6·70	7·23
60	0·8861	3·77	5·21	5·60	6·21	6·50	7·00
80	0·8710	3·63	5·10	5·49	6·04	6·36	6·82
100	0·8555	3·55	5·05	5·45	5·96	6·22	6·69
120	0·8393	3·53	5·03	5·43	5·91	6·12	6·41

d-β-Octyl glutarate.

t°.	D_4^t	[α]6438°	[α]5461°	[α]5086°	[α]4800°	[α]4678°	[α]4358°
20°	0·9161	7·12°	10·35°	11·63°	12·77°	13·39°	15·35°
40	0·9005	6·33	9·18	10·17	11·14	11·89	13·40
60	0·8851	5·70	8·25	9·06	9·95	10·60	11·93
80	0·8700	5·22	7·47	8·28	9·04	9·61	10·99
100	0·8543	4·87	6·91	7·72	8·43	8·96	10·25
120	0·8388	4·60	6·46	7·20	7·99	8·47	9·59

d-β-Octyl adipate.

t°.	D_4^t	[α]5893°	[α]5461°	[α]4358°
20°	0·9135	11·23°	12·66°	19·93°
40	0·8984	10·42	11·64	18·34
60	0·8832	9·55	10·69	16·93
80	0·8682	8·69	9·81	15·52
100	0·8530	7·90	9·01	14·23
120	0·8380	7·19	8·23	13·17

d-β-Octyl pimelate.

t°.	D_4^t	[α]6438°	[α]5461°	[α]5086°	[α]4800°	[α]4678°	[α]4358°
20°	0·9105	9·53°	13·18°	15·33°	17·22°	18·25°	20·64°
40	0·8954	8·49	11·52	13·34	14·10	16·10	17·94
60	0·8810	7·72	10·31	11·83	13·39	14·16	15·91
80	0·8666	7·13	9·42	10·80	12·28	12·99	14·40
100	0·8518	6·76	8·83	10·14	11·62	12·21	13·48
120	0·8363	6·53	8·44	9·66	11·26	11·79	12·94

d-β-Octyl suberate.

t°.	D_4^t	[α]5893°	[α]5461°	[α]4358°
20°	0·9084	11·01°	12·95°	19·59°
40	0·8937	9·89	11·59	17·97
60	0·8789	8·85	10·47	16·77
80	0·8642	8·03	9·54	15·79
100	0·8493	7·35	8·95	14·84
120	0·8346	6·85	8·46	13·88

d-β-Octyl azelate.

t°.	D_4^t	[α]6438°	[α]5461°	[α]5086°	[α]4800°	[α]4678°	[α]4358°
20°	0·9050	9·02°	12·76°	14·69°	16·36°	17·10°	19·54°
40	0·8912	8·37	11·58	13·51	14·99	15·60	17·59
60	0·8770	7·75	10·68	12·36	13·69	14·23	16·12
80	0·8627	7·16	9·85	11·33	12·57	13·07	14·84
100	0·8485	6·64	9·17	10·40	11·50	12·01	13·84
120	0·8340	6·23	8·58	9·59	10·60	11·05	12·93

TABLE IV (continued).

Densities and Rotatory Powers of the Esters.

d-β-Octyl sebacate.

t°.	$D_4^{t°}$	$[\alpha]_{5893}$	$[\alpha]_{5461}$	$[\alpha]_{5086}$	$[\alpha]_{4800}$	$[\alpha]_{4678}$	$[\alpha]_{4358}$
20°	0·9038	8·45°	12·04°	14·16°	15·80°	16·75°	18·87°
40	0·8897	7·64	10·84	12·75	14·03	14·86	16·86
60	0·8752	6·95	9·76	11·43	12·48	13·35	15·04
80	0·8611	6·39	8·83	10·36	11·29	12·08	13·51
100	0·8470	5·95	8·03	8·40	10·34	11·10	12·26
120	0·8326	5·62	7·45	8·72	9·61	10·31	11·29

d-β-Octyl n-undecane-α-dicarboxylate.

t°.	$D_4^{t°}$	$[\alpha]_{5893}$	$[\alpha]_{5461}$	$[\alpha]_{4358}$
20°	0·8975	9·25°	11·12°	17·47°
40	0·8827	8·77	10·35	16·02
60	0·8680	8·48	9·75	14·79
80	0·8533	8·27	9·33	13·78
100	0·8386	8·02	8·95	12·83
120	0·8237	7·89	8·74	11·99

d-β-Octyl ethyl malonate.

t°.	$D_4^{t°}$	$[\alpha]_{5893}$	$[\alpha]_{5461}$	$[\alpha]_{4358}$
20°	0·9596	9·27°	10·83°	17·40°
40	0·9415	8·10	9·28	15·19
60	0·9234	7·36	8·41	13·74
80	0·9054	6·67	7·73	12·59
100	0·8872	6·13	7·17	11·61
120	0·8691	5·66	6·72	10·81

d-β-Octyl n-nonane-α-dicarboxylate.

$D_4^{t°}$	$[\alpha]_{5893}$	$[\alpha]_{5461}$	$[\alpha]_{4358}$
0·9027	10·37°	11·77°	18·30°
0·8882	9·39	10·54	16·05
0·8737	8·63	9·66	14·65
0·8594	7·84	8·87	13·43
0·8448	7·08	8·05	12·33
0·8303	6·29	7·18	11·27

d-β-Octyl methyl oxalate.

$D_4^{t°}$	$[\alpha]_{5893}$	$[\alpha]_{5461}$	$[\alpha]_{4358}$
0·9840	14·22°	16·64°	25·91°
0·9656	13·32	15·24	24·25
0·9471	12·72	14·42	22·96
0·9285	12·22	13·77	21·96
0·9100	11·70	13·21	21·01
0·8915	11·39	12·68	20·19

l-β-Octyl methyl succinate.

$D_4^{t°}$	$[\alpha]_{5893}$	$[\alpha]_{5461}$	$[\alpha]_{4358}$
0·9672	−3·54°	−3·97°	−5·85°
0·9501	3·39	3·83	5·62
0·9331	3·30	3·71	5·42
0·9160	3·12	3·56	5·20
0·8991	2·94	3·38	5·00
0·8822	2·77	3·17	4·78

d-β-Octyl n-decane-α-dicarboxylate.

$D_4^{t°}$	$[\alpha]_{5893}$	$[\alpha]_{5461}$	$[\alpha]_{4358}$
0·9031	10·36°	11·29°	16·98°
0·8887	9·25	10·22	15·37
0·8744	8·42	9·40	14·32
0·8599	7·67	8·70	13·42
0·8455	7·02	8·02	12·56
0·8307	6·52	7·44	11·70

d-β-Octyl ethyl oxalate.

$D_4^{t°}$	$[\alpha]_{5893}$	$[\alpha]_{5461}$	$[\alpha]_{4358}$
0·9638	13·98°	16·33°	24·94°
0·9453	13·05	15·13	23·56
0·9269	12·54	14·17	22·08
0·9085	12·48	13·72	21·04
0·8902	12·38	13·44	20·08
0·8718	12·37	13·36	19·21

d-β-Octyl ethyl succinate.

$D_4^{t°}$	$[\alpha]_{5893}$	$[\alpha]_{5461}$	$[\alpha]_{4358}$
0·9600	4·37°	3·67°	2·44°
0·9425	4·16	3·48	2·29
0·9252	3·98	3·39	2·25
0·9080	3·88	3·35	2·20
0·8912	3·79	3·30	2·20
0·8740	3·75	3·30	2·20

TABLE V.

Determinations of Rotatory Power in approximately 5 per cent. Solution.

Ester.	In ethyl alcohol.							In carbon disulphide.							
	Grams of ester in 100 c.c. of solution.	Temp.	a_{5893}	a_{5461}	a_{4358}	$[a]_{5893}$	$[a]_{5461}$	Grams of ester in 100 c.c. of solution.	Temp.	a_{5893}	a_{5461}	a_{4358}	$[a]_{5893}$	$[a]_{5461}$	$[a]_{4358}$
.β-Octyl oxalate	4·99	18°	2·37°	2·75°	4·36°	23·73°	27·54°	4·97	16°	1·03°	1·37°	1·71°	10·37°	13·79°	17·22°
malonate	5·04	,,	0·97	1·06	1·62	9·63	10·52	4·99	17	−1·31	−1·51	−3·01	−13·13	−15·14	−30·17
succinate	5·10	,,	0·18	0·17	−0·03	1·77	1·67	5·03	,,	−2·13	−2·51	−5·01	−21·18	−24·97	−49·82
glutarate	5·07	,,	0·85	0·96	1·47	8·39	9·48	5·05	,,	−1·18	−1·38	−2·76	−11·69	−13·67	−27·33
adipate	5·03	,,	0·95	1·04	1·68	9·45	10·35	5·11	,,	−1·12	−1·34	−2·73	−10·95	−13·10	−26·70
pimelate	5·04	,,	0·95	1·11	1·81	9·43	11·03	5·09	18	−0·90	−1·21	−2·32	−8·85	−11·00	−22·81
suberate	5·03	19	0·90	1·08	1·78	8·95	10·74	5·01	,,	−0·96	−1·13	−2·05	−9·59	−11·29	−20·48
azelate	5·15	,,	0·95	1·12	1·66	9·22	10·86	5·03	,,	−0·79	−0·98	−2·03	−7·86	−9·75	−20·19
sebacate	5·00	13	0·87	1·04	1·68	8·71	10·41	4·96	,,	−0·80	−1·02	−2·02	−8·06	−10·28	−20·34
n-nonane-α-α-dicarboxylate	5·04	,,	0·90	1·02	1·65	8·93	10·12	4·97	,,	−0·77	−0·94	−2·01	−7·75	−9·46	−20·22
n-decane-α-α-dicarboxylate	5·01	19	0·93	1·00	1·66	9·29	9·98	4·97	,,	−0·76	−0·93	−1·88	−7·65	−9·36	−18·94
n-undecane-α-α-dicarboxylate	4·62	,,	0·87	0·93	1·40	9·41	10·06	4·71	,,	−0·59	−0·74	−1·46	−6·26	−7·85	−15·50
,β-Octyl methyl oxalate	4·95	20	1·30	1·61	2·41	13·14	16·28	4·57	20	1·05	1·14	1·67	11·48	12·47	18·27
ethyl oxalate	4·99	18	1·36	1·80	2·56	13·61	18·03	5·01	18	1·00	1·21	1·85	9·98	12·08	18·47
ethyl malonate	5·04	21	0·74	0·82	1·38	7·34	8·14	5·06	19·5	−0·51	−0·71	−1·48	−5·04	−7·01	−14·62
-β-Octyl methyl succinate	5·05	20	−0·13	−0·22	−0·30	−1·29	−2·18	5·06	20	1·28	1·62	3·19	12·66	16·02	31·54
l,β-Octyl ethyl succinate	5·07	19	0·19	0·27	0·48	1·87	2·66	4·99	17	−1·33	−1·49	−3·10	−13·34	−14·94	−31·09

oxylate, b. p. 205—210°/1 mm.; and n-undecanedicarboxylate, b. p. 215—217°/2 mm.

The last ester in the list solidified on keeping to a mass of colourless plates which melt at 21°.

The esters were not analysed in the usual way, as agreement between the experimentally determined and the calculated values of the molecular refraction was considered to be a more satisfactory criterion of purity.

Density determinations were carried out between 20° and 130°, a carefully calibrated pyknometer of about 3 c.c. capacity being used.

Refractive indices were determined at a constant temperature for light of several wave-lengths by means of a refractometer of the Pulfrich type.

The polarimetric measurements were made in a 50 mm. jacketed tube round which mineral oil was circulated by means of a pump. Observations were made from 20° to about 140° at temperature intervals of about 20°, but in Table III rotations are given as for a 1-dcm. tube.

That no racemisation had occurred during the preparation of the esters or during their subsequent heating or treatment with solvents was proved by the fact that all the esters on subsequent hydrolysis yielded *sec.*-octyl alcohol of maximum rotation.

For observations of rotatory power in solution, about 1 gram of the active ester was dissolved in the solvent and the solution made up to 20 c.c. at the temperature of the laboratory. Determinations of rotatory power were made in a 2-dcm. tube.

V.—*Investigations on the Dependence of Rotatory Power on Chemical Constitution. Part XVII. A New Type of Walden Inversion.*

By HENRY PHILLIPS.

IN the examples of the Walden inversion so far recorded, an entire group attached to the asymmetric carbon atom of an optically active compound suffers two or more displacements. By this

means either the same compound of opposite configuration is obtained or, by conducting one displacement under two different sets of conditions, products are obtained which are opposite in sign :

$$l\text{-Malic acid} \xrightarrow{\text{PCl}_5} d\text{-Chlorosuccinic acid} \underset{\overrightarrow{\text{KOH}}}{\overset{\text{Ag}_2\text{O}}{\diagup\diagdown}} \begin{array}{l} d\text{-Malic acid} \\ l\text{-Malic acid} \end{array}$$
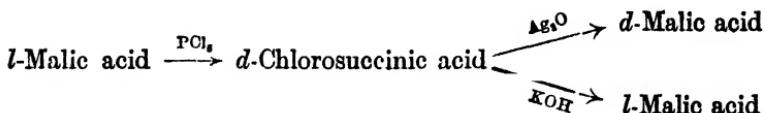
The above scheme, due to Walden (*Ber.*, 1896, **29**, 113), illustrates both types. They are, therefore, processes occurring in two stages. At one of these stages an " abnormal " reaction occurs resulting in a change of configuration, but at which one it is impossible to decide. In both reactions a group attached to the asymmetric carbon atom is replaced. Does the entering group in the first displacement take up the same position relative to the three remaining groups as that vacated by the group displaced? The sign of rotation of the product cannot be relied upon to give a correct answer to this question. Many instances are known in which substitution occurs remote from the asymmetric carbon atom, yet produces a reversal of sign. In such cases no change of configuration can be assumed, and therefore it is evident that change of sign does not necessarily coincide with change of configuration.

Attempts have been made to overcome this difficulty and to provide a method of determining whether a given reaction is abnormal from a consideration of the mechanism of the reactions in question by, *inter alios*, Armstrong (T., 1896, **69**, 1399), Gadamer (*Chem. Ztg.*, 1910, **34**, 1004), and Biilmann (*Annalen*, 1911, **388**, 338). Further, Clough (T., 1918, **113**, 526) has suggested certain principles by which the relative configurations of similarly constituted compounds can be determined.

In the examples of the Walden inversion to be described, however, we can on general grounds single out the particular reactions which occur with configurational change. When *d*-benzylmethylcarbinol is allowed to react with *p*-toluenesulphonyl chloride in the presence of pyridine, benzylmethylcarbinyl *p*-toluenesulphonate is obtained.

$$\begin{array}{c} C_6H_5\cdot CH_2 \\ CH_3 \end{array}\!\!\!>\!\!C\!<\!\!\!\begin{array}{c} O\,H \\ H \end{array} + Cl\cdot SO_2\cdot C_7H_7$$
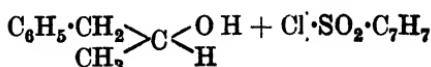
In this reaction, complete substitution of a group attached to the asymmetric carbon atom does not occur, the hydrogen atom of the hydroxyl group alone suffers displacement. It is justifiable

therefore, to refer to the sulphonic ester prepared in this way from the dextrorotatory alcohol as the d-sulphonate, and it is interesting to note that when this is dissolved in benzene, chloroform, ethyl alcohol, carbon disulphide, or pyridine, the solutions obtained are all dextrorotatory.

When this d-sulphonate is treated with sodium ethoxide in benzene or, better, heated under reflux in absolute alcoholic solution in the presence of solid potassium carbonate, the ethyl ether of benzylmethylcarbinol is formed and has in this case a lævo-rotation.

If, however, d-benzylmethylcarbinol be converted into its potassium derivative and the latter allowed to react with ethyl p-toluenesulphonate, the ethyl ether of benzylmethylcarbinol produced has a dextrorotation.

$$\begin{array}{ccc}
\underset{\text{(i.)}}{\overset{C_6H_5 \cdot CH_2}{\underset{CH_3}{}}} \!\!>\!\! C \!\!<\!\! \overset{OH}{H} & \rightarrow & \overset{C_6H_5 \cdot CH_2}{\underset{CH_3}{}} \!\!>\!\! C \!\!<\!\! \overset{O \cdot SO_2 \cdot C_7H_7}{H} \xrightarrow{\underset{K_2CO_3}{EtOH}} & \overset{C_6H_5 \cdot CH_2}{\underset{CH_3}{}} \!\!>\!\! C \!\!<\!\! \overset{H}{OEt}
\end{array}$$

$\alpha_{5461}^{22°} + 33 \cdot 02°$ (for 100 mm).

Dextro rotation and -configuration.

$[\alpha]_{5461} + 31 \cdot 11°$ (in benzene ; $c = 5$).

Dextro-rotation and -configuration.

$\alpha_{5461}^{23°} - 19 \cdot 90°$ (for 100 mm.).

Lævo-rotation and -configuration.

$$\begin{array}{ccc}
\underset{\text{(ii.)}}{\overset{C_6H_5 \cdot CH_2}{\underset{CH_3}{}}} \!\!>\!\! C \!\!<\!\! \overset{OEt}{H} & \xleftarrow{EtBr} \overset{C_6H_5 \cdot CH_2}{\underset{CH_3}{}} \!\!>\!\! C \!\!<\!\! \overset{OK}{H} \xrightarrow{EtO \cdot SO_2 \cdot C_7H_7} & \overset{C_6H_5 \cdot CH_2}{\underset{CH_3}{}} \!\!>\!\! C \!\!<\!\! \overset{OEt}{H}
\end{array}$$

$\alpha_{5461}^{23°} + 23 \cdot 50°$ (for 100 mm.)

Dextro-rotation and -configuration.

$\alpha_{5461}^{22 \cdot 5} + 19 \cdot 84°$ (for 100 mm.).

Dextro-rotation and -configuration.

What is the sign of rotation of the ethyl ether which corresponds in configuration to the d-alcohol? This can be decided by the fact that the potassium derivative of the d-alcohol gives a dextrorotatory ethyl ether when treated with ethyl bromide, a reaction in which configurative change is unlikely to occur.

In the first series of reactions, however, the lævorotatory ethyl ether of benzylmethylcarbinol is obtained from the dextrorotatory sulphonate, which can be said to have the same configuration as d-benzylmethylcarbinol. The conclusion can therefore be drawn that when the dextrorotatory sulphonate reacts with ethyl alcohol in the presence of potassium carbonate, the l-ethyl ether of benzylmethylcarbinol is produced, the configuration of which is the opposite to that of the dextrorotatory sulphonate used.

This is a definite change in configuration in one stage and therefore it is a definitely " abnormal " reaction.

How does this conclusion agree with the usually adopted views

of the mode of reaction of sulphonic esters? Ferns and Lapworth (T., 1912, **101**, 273) have shown that the reactions of these esters resemble very closely those of the alkyl haloids.

$$\text{(I.)} \quad \begin{matrix} C_6H_5 \cdot CH_2 \\ CH_3 \end{matrix} > C < \begin{matrix} H \\ O \cdot SO_2 \cdot C_7H_7 \\ {}^*EtO \vdots H \\ + K_2CO_3 \end{matrix} \qquad \text{(II.)} \quad \begin{matrix} C_6H_5 \cdot CH_2 \\ CH_3 \end{matrix} > C < \begin{matrix} H \\ O \vdots K \\ Et \vdots O \cdot SO_2 \cdot C_7H_7 \end{matrix}$$
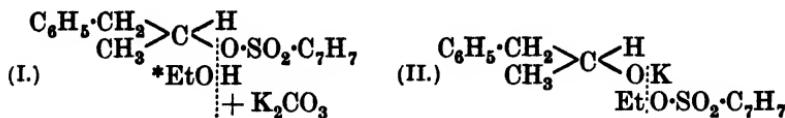
Adopting these views, it is apparent that in reaction I, involving the complete replacement of a group from the asymmetric carbon atom, change of configuration is possible, but in reaction II, in which bonds of the asymmetric carbon atom remain undisturbed, it is unlikely. This is in agreement with the results obtained.

On examination of the magnitudes of the rotations of the ethyl ethers of benzylmethylcarbinol obtained by the three separate methods another important conclusion can be drawn. The "abnormal" reaction occurs with almost complete configurative change. The rotatory power of the ether prepared from the potassium derivative of the alcohol and ethyl bromide is higher than that of the ether prepared by the other two methods, in which a loss in rotatory power might be suspected.

It was decided to extend the investigation and endeavour to prepare a compound from d-benzylmethylcarbinyl p-toluene-sulphonate with complete change of configuration. For such a purpose the compound should be one from which the alcohol could be recovered by methods not likely to cause racemisation or con-figurative change, so that the rotation of the recovered alcohol could be compared with that of the original. It was found that such compounds, for example, benzylmethylcarbinyl esters of carboxylic acids, could be readily prepared by the interaction of the potassium salts of these acids and the p-toluenesulphonate in alcoholic solution. Lævorotatory benzylmethylcarbinyl acetate was prepared from pure d-benzylmethylcarbinol by the following cycle of reactions:

$$\begin{matrix} C_6H_5 \cdot CH_2 \\ CH_3 \end{matrix} > C < \begin{matrix} H \\ OH \end{matrix} \quad \rightarrow \quad \begin{matrix} C_6H_5 \cdot CH_2 \\ CH_3 \end{matrix} > C < \begin{matrix} H \\ O \cdot SO_2 \cdot C_7H_7 \end{matrix} \xrightarrow{\text{KO·OC·CH}_3}$$

$$\text{(III.)} \qquad\qquad\qquad\qquad \text{(IV.)}$$

$\alpha_{5461}^{25°} + 33 \cdot 02°$ (for 100 mm.). $[\alpha]_{5461} + 31 \cdot 11°$ (in benzene solution).

$$\begin{matrix} C_6H_5 \cdot CH_2 \\ CH_3 \end{matrix} > C < \begin{matrix} H \\ O \cdot CO \cdot CH_3 \end{matrix} \quad \rightarrow \quad \begin{matrix} C_6H_5 \cdot CH_2 \\ CH_3 \end{matrix} > C < \begin{matrix} H \\ OH \end{matrix}$$

$$\text{(V.)} \qquad\qquad\qquad\qquad \text{(VI.)}$$

$\alpha_{5461}^{25°} - 7 \cdot 06°$ (for 100 mm.). $\alpha_{5461}^{25°} - 32 \cdot 18°$ (for 100 mm.).
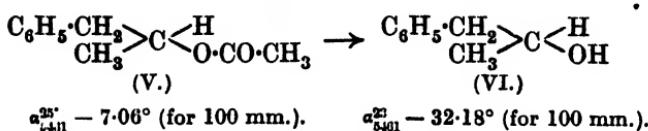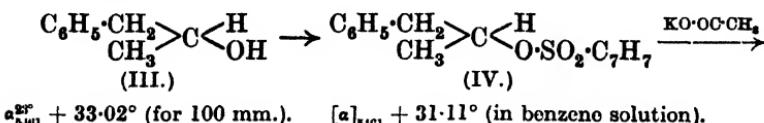
* Or sodium ethoxide.

The esters derived from d-benzylmethylcarbinol and the normal aliphatic acids have been prepared and their optical properties fully described in Part VIII of these investigations (T., 1914, **105**, 2261). The acetate prepared from the d-alcohol by the action of acetic anhydride is dextrorotatory ($\alpha_{5461}^{25°} + 7·13°$ *) and on hydrolysis with alcoholic sodium hydroxide yields the d-alcohol of unchanged rotatory power. That both these reactions should be accompanied by *complete* configurative change is unlikely and hence it may be assumed that dextrorotatory benzylmethylcarbinyl acetate has the same configuration as the dextrorotatory alcohol. In the above cycle of reactions, however, this ester is obtained with a lævorotation from a dextrorotatory sulphonate, the configuration of which can be said to be dextro.

The passage from IV to V therefore occurs by a definitely abnormal reaction, and the almost complete inversion of configuration is clearly demonstrated by these reactions.

The l-ethyl ether of benzylmethylcarbinol was also formed during the preparation of the acetate, being produced by the interaction of the d-sulphonate and ethyl alcohol, used as the reaction medium, in the presence of potassium acetate. It had $\alpha_{5461}^{21} - 21·92°$, being higher in rotation than that prepared previously. Its presence necessitated very careful fractional distillation of the product, since the boiling points of the acetate and of the ethyl ether are fairly close.

To ensure that the ester obtained was uncontaminated with this ether, a further series of reactions was undertaken in which the n-valerate was substituted for the corresponding acetate.

In these reactions, a specimen of l-benzylmethylcarbinol with $\alpha_{5461}^{21} - 24·94°$ was converted through the corresponding sulphonate into the n-valerate, which had $\alpha_{5461}^{16.5} + 9·76°$ and gave when hydrolysed a d-alcohol with $\alpha_{5461}^{20} + 23·98°$. Again the loss in rotatory power was small and complete confirmation of the other reaction was thus obtained.

Ferns and Lapworth (*loc. cit.*) also raise another point which is of interest. Discussing the reaction which occurs between phenyl p-toluenesulphonate and sodium ethoxide, they point out that in this case it must be regarded as occurring in two stages :

$$C_6H_5 \cdot O\,SO_2 \cdot C_7H_7 + Na\,OEt \longrightarrow C_6H_5 \cdot ONa + EtO \cdot SO_2 \cdot C_7H_7$$

$$C_6H_5 \cdot O\,Na + Et\,O \cdot SO_2 \cdot C_7H_7 \longrightarrow EtO \cdot C_6H_5 + NaO \cdot SO_2 \cdot C_7H_7.$$
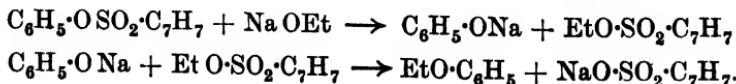
The reasons they advance are first that the reaction proceeds readily, a fact which does not seem to indicate the breakage of

* All observed rotations recorded in this paper are for 100 mm.

an O-C linking the carbon of which forms part of a benzene nucleus; and secondly, that in none of its simpler reactions does phenyl p-toluenesulphonate reveal the O-C linking as the weakest part of its structure. For example, it does not yield aniline on treatment with ammonia.

During this investigation it was also observed that phenyl p-toluenesulphonate would not react with potassium acetate in ethyl alcoholic solution, although under the same conditions ethyl p-toluenesulphonate rapidly produced ethyl acetate.

As an explanation of the reaction, Ferns and Lapworth put forward the suggestion, outlined above, that an exchange of radicles occurs, an O-S linking breaking in the process, and the sodium phenoxide and ethyl p-toluenesulphonate produced reacting in the usual manner.

Assuming this explanation to be correct and applying it to the reaction between the potassium derivative of l-benzylmethylcarbinol and phenyl p-toluenesulphonate, we should expect the following sequence of reactions to take place:

A. $\overset{l.*}{\underset{CH_3}{C_6H_5 \cdot CH_2}} > C < \overset{H}{\underset{O \cdot K}{}} + C_6H_5 \cdot O \vdots SO_2 \cdot C_7H_7 \longrightarrow$

$\overset{l.}{\underset{CH_3}{C_6H_5 \cdot CH_2}} > C < \overset{H}{\underset{O \cdot SO_2 \cdot C_7H_7}{}} + C_6H_5 \cdot OK$

B. $C_6H_5 \cdot O K + \underset{CH_3}{C_6H_5 \cdot CH_2} > C < \overset{H}{\underset{O \cdot SO_2 \cdot C_7H_7}{}} \longrightarrow$

$\underset{\underset{d.*}{CH_3}}{\overset{l.}{C_6H_5 \cdot CH_2}} > C < \overset{H}{\underset{O \cdot C_6H_5}{}} + KO \cdot SO_2 \cdot C_7H_7$
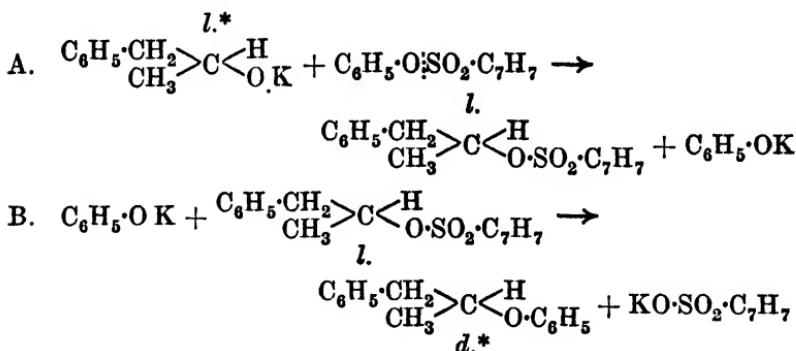
Since we have adopted the suggestion that an exchange of radicles occurs as indicated by the dotted lines in A, the potassium derivative of the l-alcohol and phenyl p-toluenesulphonate will give rise to l-benzylmethylcarbinyl p-toluenesulphonate and potassium phenoxide. These products will react (B) and the phenyl ether of benzylmethylcarbinol will be produced with inversion of configuration, it being assumed that sodium ethoxide and potassium phenoxide react in an identical manner with the l-sulphonate.

Two experiments could therefore be performed. The potassium derivative of the l-alcohol could be allowed to react with phenyl p-toluenesulphonate (A), or potassium phenoxide with l-benzylmethylcarbinyl p-toluenesulphonate (B). They would virtually

* $l.$ and $d.$ *configurations.*

be identical reactions, the phenyl ether of the alcohol being produced during each experiment with inversion of configuration, and therefore the sign of rotation of the ethers obtained should be the same.

Should, however, the explanation be incorrect, that is, should phenyl p-toluenesulphonate react in the same manner as ethyl p-toluenesulphonate, it would, when treated with the potassium derivative of the l-alcohol, produce a phenyl ether *without* configurative change; and there would result in the two experiments outlined above phenyl ethers of *opposite sign*.

Experimentally it was found that whether the reaction was commenced as indicated in A, or, its course being anticipated, as in B,* the phenyl ethers produced had the same sign of rotation, both being dextrorotatory.

If, therefore, the assumption is made that potassium phenoxide and sodium ethoxide react in the same manner with the l-sulphonate, these two experiments give considerable support to the view of the mode of reaction of phenyl p-toluenesulphonate put forward by Ferns and Lapworth.

Discussion of Results.

McKenzie and Clough (T., 1913, **103**, 687), by effecting the interconversion of the optically active phenylmethylcarbinols, showed for the first time that the phenomenon of the Walden inversion was not confined to compounds containing a carboxyl or carboalkyloxy-group. Research on the Walden inversion has, however, been mainly confined to carboxylic acids containing also an amino- or a hydroxy-group, or a halogen atom. During the reactions of these compounds involving the complete removal of a group attached to the asymmetric carbon atom a certain amount of " displacement " racemisation (Senter, Drew, and Martin, T., 1918, **113**, 156) occurs. The compounds are also liable in some cases to undergo "catalytic" racemisation, which renders their isolation and purification without loss of rotatory power difficult. When, therefore, the optical enantiomorph of such compounds is obtained after two displacement reactions, a determination of its rotatory power does not truly indicate to what extent the " abnormal " reaction predominates.

If, however, the series of reactions described in the interconversion of the enantiomorphously related benzylmethylcarbinols be examined, it will be seen that, throughout, the compounds involved are stable both as regards their chemical and their optical pro-

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* Using, however, sodium phenoxide instead of potassium phenoxide.

perties. They are compounds which can withstand without catalytic racemisation the experimental conditions to which they are subjected, and also at one stage only (the interaction between the d-sulphonate and potassium acetate) is any displacement racemisation likely to occur.

To this fact is partly due the observed completeness of inversion, and, moreover, it points to the stage at which the "abnormal" reaction occurs as the source of the very slight decrease in rotatory power, which is approximately 2 per cent.

This decrease is so small that it must be carefully borne in mind during any attempt to explain the mechanism of this particular reaction. The tendency for the reaction to occur in a definite manner accompanied by inversion of configuration is obviously overwhelming. In other words, it can be said that the group entering the asymmetric molecule is compelled to occupy only one position relative to the other three, and this is a position which entails configurative change.

This position, it seems possible to assume, corresponds to a portion of the surface of the asymmetric carbon atom which is potentially unsaturated. An examination of the constitutional formula (VII), together with a knowledge of the fact that the sulphonic ester exhibits a strong tendency to lose the elements of the corresponding sulphonic acid, enables this possibility to be visualised.
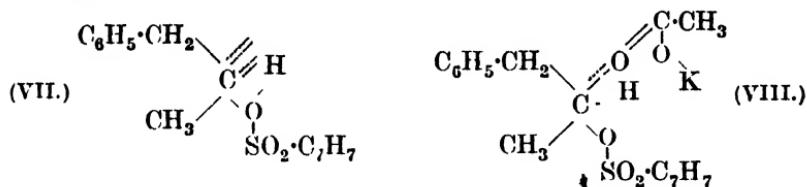
It is postulated that under certain conditions, such as increase of temperature, the sulphonic ester molecule assumes an active condition, arising through the weakening of the attachment of the α-hydrogen atom to the asymmetric carbon atom; this weakening being due to the ester oxygen atom of the $O \cdot SO_2 \cdot C_7H_7$ group exerting its residual valencies.

The ester molecule, then, in its active condition contains a hydrogen atom held partly by the residual valencies of the ester oxygen atom and partly by the valency of the asymmetric carbon atom. Thus the portion of the latter atom to which the hydrogen is now but loosely linked is in possession of residual valency. It is postulated that, in an alcoholic solution of potassium acetate, an indirect "abnormal" reaction takes place by the addition of

a molecule of potassium acetate to this unsaturated portion through the agency of the carbonyl oxygen atom which it contains (VIII).

The α-hydrogen atom is displaced by the potassium and the acetyl group usurps the whole affinity of the portion of the asymmetric carbon atom to which it was previously only loosely attached. The potassium p-toluenesulphonate formed during this displacement leaves the molecule, the hydrogen liberated during its formation occupying the position thus vacated (IX).

$$
\begin{array}{ll}
\underset{\text{(IX.)}}{\underset{\mathrm{CH_3}}{\overset{\mathrm{C_6H_5 \cdot CH_2}}{\diagdown}}\underset{\diagdown \mathrm{H}}{\overset{\diagup}{\mathrm{C}}}\!\!O\!\!\overset{\displaystyle \mathrm{C \cdot CH_3}}{\underset{\underset{\mathrm{SO_2 \cdot C_7H_7}}{\overset{|}{\mathrm{O}}}}{\underset{\mathrm{K}}{\overset{\mathrm{O}}{}}}}}
&
\underset{\mathrm{SO_2 \cdot C_7H_7}}{\underset{\mathrm{CH_3}}{\overset{\mathrm{C_6H_5 \cdot CH_2}}{\diagdown}}\overset{\diagup}{\underset{\diagdown \mathrm{O}}{\mathrm{C}}}\!\!=\!\!H} \quad \underset{\text{(X.)}}{\mathrm{K\!-\!O \cdot CO \cdot CH_3}}
\end{array}
$$
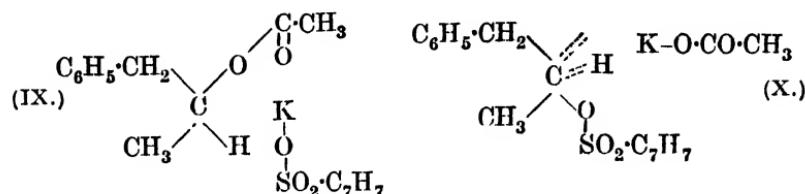
It is suggested also that a direct reaction can occur, to an extent sufficient to account for the observed loss of rotatory power. Commencing as before with the molecule of the sulphonic ester in an active condition, it is assumed that it is approached by a molecule of potassium acetate, possibly in an ionised condition (X). No addition occurs at the unsaturated portion of the surface of the asymmetric carbon atom, but instead, the potassium atom displaces the α-hydrogen atom, which assumes its normal state and position in the molecule (XI).

$$
\begin{array}{ll}
\underset{\text{(XI.)}}{\underset{\mathrm{CH_3}}{\overset{\mathrm{C_6H_5 \cdot CH_2}}{\diagdown}}\overset{\diagup \mathrm{H}}{\underset{\underset{\mathrm{SO_2 \cdot C_7H_7}}{\overset{|}{\mathrm{O}}}}{\mathrm{C}}}} \;\; \underset{\overset{|}{\mathrm{O}}}{\mathrm{K}} \; \mathrm{O \cdot CO \cdot CH_3}
&
\underset{\text{(XII.)}}{\underset{\mathrm{CH_3}}{\overset{\mathrm{C_6H_5 \cdot CH_2}}{\diagdown}}\overset{\diagup \mathrm{H}}{\underset{\underset{\mathrm{CO \cdot CH_3}}{\overset{|}{\mathrm{O}}}}{\mathrm{C}}}} \; + \mathrm{KO \cdot SO_2 \cdot C_7H_7}
\end{array}
$$
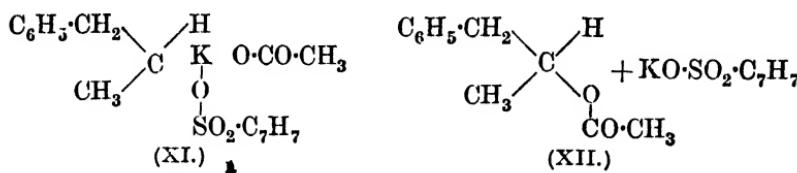
Potassium p-toluenesulphonate is then eliminated from the molecule, leaving the acetyl group to enter the position vacated by the group $\mathrm{O \cdot SO_2 \cdot C_7H_7}$ (XII).

This would leave an acetic ester of the same configuration as the original sulphonic ester.

In each of these hypothetical molecular interactions the formation of potassium p-toluenesulphonate in the complex and its subsequent departure do not necessarily imply that only three valencies of the asymmetric carbon atom are utilised at any particular instant. This salt, when formed, can still remain momentarily attached by the residual valencies of the ester oxygen, and moreover the portion of the asymmetric carbon atom by which it is thus loosely held would be in a partly unsaturated condition.

It would therefore be likely that the atom or group set free through the formation of potassium p-toluenesulphonate would be attracted to this position. The arrangement within the bimolecular complexes before final disruption occurs can therefore be represented as follows :
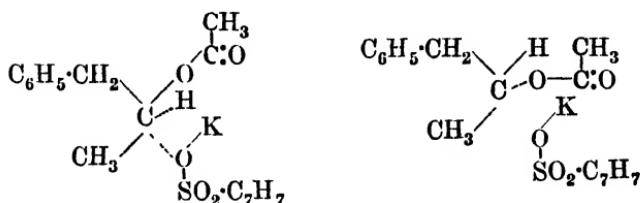
It is conceivable that a certain proportion of such molecular interactions may miscarry at one or other of the stages through which, it is suggested, they pass, and in such cases an unsaturated hydrocarbon will result.

Experimental evidence of the formation of varying amounts of an unsaturated hydrocarbon has been obtained; in attempting to prepare the ethyl ether of benzylmethylcarbinol from the corresponding sulphonate, if sodium ethoxide be used instead of potassium carbonate, the product consists almost entirely of such a compound, this being due presumably to the too rapid withdrawal of the elements of the sulphonic acid from the molecule.

It will be noticed also that the explanation of these reactions depends on the presence in the ester molecule of a detachable hydrogen atom linked to the same carbon atom as the $O \cdot SO_2 \cdot C_7 H_7$ group.

From these assumptions it would follow that ethyl p-toluenesulphonate, $CH_3 \cdot CH_2 \cdot O \cdot SO_2 \cdot C_7 H_7$, should react readily with potassium acetate in alcoholic solution, whilst phenyl p-toluenesulphonate, $C_6 H_5 \cdot O \cdot SO_2 \cdot C_7 H_7$, should only react with difficulty, if at all. This conclusion is completely borne out by experiment.

An explanation is still required to account for the slight loss of rotatory power observed during the reactions involved in the preparation of the ethyl ethers.

In this connexion it is noteworthy that the loss of rotatory power is the same, whether these compounds are prepared through the agency of the sulphonic ester of the optically active alcohol, or of ethyl p-toluenesulphonate. This case therefore permits of a different explanation from that advanced in the case of the esters.

Bearing in mind the supposed anomalous behaviour of phenyl p-toluenesulphonate (p. 49), it is postulated that, in the reaction between ethyl p-toluenesulphonate and the potassium derivative of

benzylmethylcarbinol, there is a tendency for an exchange of radicles to occur :

$$C_2H_5 \overset{\cdot}{\big|} \cdot O \cdot SO_2 \cdot C_7H_7 + K \overset{d.}{\big|} O - CH \big< \begin{matrix} CH_2 \cdot C_6H_5 \\ CH_3 \end{matrix} \rightleftharpoons$$

d-Ether.

$$C_7H_7 \cdot SO_2 \cdot O \overset{d.}{\big|} CH \big< \begin{matrix} CH_2 \cdot C_6H_5 \\ CH_3 \end{matrix} + C_2H_5 \cdot O \overset{}{\big|} K$$

l-Ether.
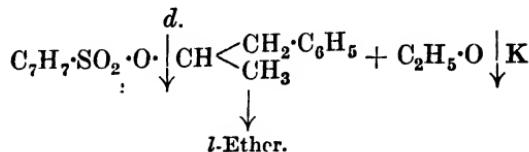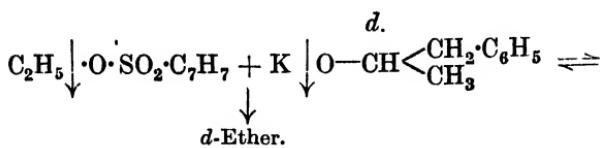
The sulphonic ester exercises its ability to decompose with breakage of an O-S linking and the exchange occurs as indicated by the dotted lines. That the amount of interchange would be small is accounted for by the ease with which ethyl *p*-toluene-sulphonate reacts with the potassium derivative of the alcohol and hence the rapidity with which the *d*-ether is produced. The yield of *l*-ethyl ether from the right-hand side of the equation will necessarily be small, but since the "abnormal" reaction results in a product of almost full activity, the amount produced need not be large to cause the small loss of rotatory power observed.

This explanation is presumed to be equally applicable to the interaction of *d*-benzylmethylcarbinyl *p*-toluenesulphonate and ethyl alcohol in the presence of potassium carbonate.

$$\begin{matrix} C_6H_5 \cdot CH_2 \\ CH_3 \end{matrix} \big> CH \overset{d.}{\big|} \cdot O \cdot SO_2 \cdot C_7H_7 + EtO \big| H \rightleftharpoons$$

l-Ether.

$$Et \big| O \cdot SO_2 \cdot C_7H_7 + \begin{matrix} C_6H_5 \cdot CH_2 \\ CH_3 \end{matrix} \overset{d.}{\big>} CH \cdot O \big| H$$
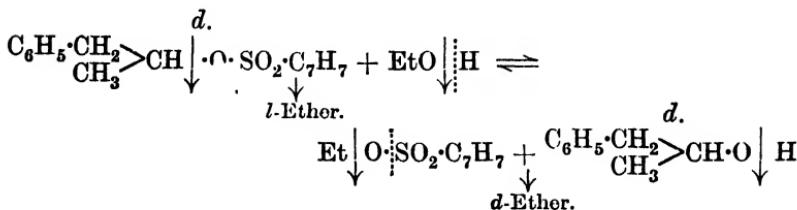
d-Ether.

In the above formulæ the dotted lines indicate the method of exchange and the arrows the double decomposition.

Again, it is evident that the extent to which reaction takes place between substances on the right-hand side of the scheme will not be large under the conditions of the experiment. It is significant, however, that if the reaction is carried out in the presence of potassium acetate, which would react with any ethyl *p*-toluenesulphonate formed, the product has a higher rotation, that is, less *d*-ether is produced.

It will be seen that these explanations are in accordance with

the view which has been frequently advanced, that a reaction which results in configurational change proceeds indirectly, being preceded by addition, whilst a normal reaction involves direct substitution. That the decrease in rotatory power or racemisation which accompanies reactions in which the phenomenon of Walden inversion is observed is due rather to the simultaneous formation of the product possessing both d- and l-configurations has also been previously postulated. Holmberg (*Arkiv Kem. Min. Geol.*, 1916, No. 8, 6) has shown that when chlorosuccinic acid is converted into xanthosuccinic acid the reaction follows two courses simultaneously :

l-Bromosuccinic acid

$\nearrow$ d-xanthosuccinic acid

$\searrow$ d-malolactone $\longrightarrow$ l-xanthosuccinic acid
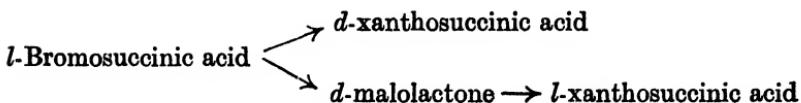
Similarly, Senter and his collaborators (T., 1915, **107**, 638 *et seq.*) showed that the action of ammonia on halogen-substituted acids yields both d- and l-amino-acids.

The explanation given of the small loss in rotatory power which accompanies the inversions described is perhaps so far based on meagre evidence. It is evident, however, that the predominance of the reaction which results in inversion of configuration prevents acceptance of the view that it occurs with racemisation. The occurrence of racemisation during a reaction suggests a haphazard interaction between two kinds of molecule. It is inconceivable that such an interaction could result in products of the degree of optical purity obtained.

EXPERIMENTAL.

d-*Benzylmethylcarbinyl* p-*Toluenesulphonate.*—This was prepared as required by the interaction in the cold of equivalent quantities of the alcohol and p-toluenesulphonyl chloride in the presence of pyridine. The reaction was complete after twelve hours. On pouring the reaction mixture into water, the ester crystallised, and after filtration was purified by recrystallisation from glacial acetic acid or ethyl alcohol. It had m. p. 94°. 0·7392 Gram of ester required 0·1007 gram of sodium hydroxide for complete hydrolysis, the theoretical amount being 0·1019 gram.

The following determinations of its optical rotatory power were made. The solutions were prepared by dissolving about one gram of the ester in the solvent and diluting to 20 c.c. The observations were taken in a 2-dcm. tube.

	Grams of solute.	Observed rotation.			$[\alpha]_\lambda$.		
Solvent.		λ 5893	λ 5461	λ 4358	λ 5893	λ 5461	λ 4358
Ethyl alcohol ...	0·5364	+1·66°	+1·84°	+3·30°	+30·90°	+34·30°	+61·37°
Benzene	1·0126	2·82	3·15	5·83	27·85	31·11	57·58
Chloroform	1·0136	2·53	3·05	5·47	24·97	30·09	53·98
Carbon disulphide	1·0046	3·09	3·75	6·87	30·76	37·33	68·28
Pyridine	0·9910	2·84	3·46	5·88	28·59	34·91	59·33

Reaction between the Potassium Derivative of d-*Benzylmethyl-carbinol and Ethyl* p-*Toluenesulphonate.*—Four grams of clean potassium were shaken in hot toluene, the latter, when cold, was replaced by 200 c.c. of dry benzene, and 15 grams of the d-alcohol were added. When dissolution of the potassium, which was hastened by gentle warming, was completed, the mixture was cooled, and 40 grams of molten ethyl p-toluenesulphonate were slowly added, a voluminous precipitate forming. When the reaction began to slow down, the mixture was shaken vigorously for twenty-two hours. It was then treated with a solution of sodium hydroxide and distilled with steam. To the benzene extract of the distillate dried with potassium carbonate, 20 grams of phthalic anhydride were added, and the solution was boiled, the benzene being allowed to distil off slowly up a fractionating column. The residue, having been heated for ten hours at 110°, was poured into dilute sodium carbonate solution, and after remaining over-night, this solution was extracted with ether. The benzylmethylcarbinyl ethyl ether obtained from the dried ethereal extract was distilled under reduced pressure, and after three fractionations 9 grams were obtained; b. p. 92—93°/19 mm., $d_4^{21°}$ 0·9168, $n_{5896}^{2°}$ 1·4848, and $\alpha_{5461}^{22·5} + 19·84°$.

Reaction between Sodium Ethoxide and Benzylmethylcarbinyl p-*Toluenesulphonate.*—The most successful experiment of this series was conducted as follows : Twenty grams of the sulphonic ester (prepared from a sample of partly active alcohol with $\alpha_{5461}^{17°} - 7·82°$ and having $[\alpha]_{5461} - 6·92°$ in benzene) were dissolved in 100 c.c. of anhydrous ethyl alcohol, and while the solution was being warmed on a water-bath a solution of 2 grams of sodium in 50 c.c. of alcohol was added during three and a half hours. The alcohol was then distilled off through a column, the residue poured into water, and the oily layer which formed extracted with ether. The product obtained from the dried ethereal extract was repeatedly distilled and gave two main fractions.

Fraction A, b. p. 62—65°/14 mm., amounted to 3 grams. It was optically inactive after four redistillations. It rapidly decolorised bromine water, had n_{5896}^{22} 1·5331, d_4^{22} 0·9045, and was an unsaturated hydrocarbon.

Fraction B, b. p. 85—88°/14 mm., closely resembled the ethyl ether of benzylmethylcarbinol. About 1·5 grams were obtained having $\alpha_{5461}^{15°}$ + 4·12°.

Reaction between d-*Benzylmethylcarbinyl* p-*Toluenesulphonate and Ethyl Alcohol in the presence of Potassium Carbonate.*—A mixture of 20 grams of the d-sulphonic ester, prepared from the pure d-alcohol, 150 c.c. of absolute alcohol, and 20 grams of dry, finely powdered potassium carbonate was heated under reflux for thirty-seven hours. The alcohol was then distilled off and the residue poured into water. The oil which separated was extracted with ether. Since benzylmethylcarbinol might have been formed during the reaction by hydrolysis of the sulphonic ester, the product was heated with phthalic anhydride for ten hours at 100—110° and poured into sodium carbonate solution, from which the required product was isolated in the usual way by extraction with ether. On distillation a very small quantity of a hydrocarbon was isolated. The main fraction, 6·9 grams, boiled at 85—100°/20 mm. After two distillations, the mixed ether (5 grams) had b. p. 92—94°/20 mm., $d_4^{22·5°}$ 0·9177, $n_{5896}^{20°}$ 1·4878, and $\alpha_{5461}^{23°}$ — 19·90°, which was unchanged by subsequent distillation.

Reaction between d-*Benzylmethylcarbinyl* p-*Toluenesulphonate and Potassium Acetate.*—Thirty grams of the pure d-ester were dissolved in 150 c.c. of absolute alcohol, and 21 grams of freshly fused potassium acetate were added. The clear solution obtained on warming soon became clouded by a gelatinous precipitate, which rapidly changed to white, crystalline plates. After six hours' heating under reflux, the alcohol was distilled off and the residue poured into water. The oil which separated was isolated with ether in the usual manner.

On distillation, a small fraction, b. p. below 100°/16 mm., was obtained, the main fraction, 14·8 grams, boiling at 100—113°/16 mm. After three fractionations, 7·8 grams of l-benzylmethylcarbinyl acetate, b. p. 112—114°/18 mm., were isolated having $d_4^{24·5°}$ 0·9978, $n_{5896}^{24°}$ 1·4881, and $\alpha_{5461}^{25°}$ — 7·06°.

On hydrolysis with sodium hydroxide, 1·0660 grams required 0·2391 gram of NaOH (theory 0·2395 gram).

The remainder of the l-acetate was hydrolysed in alcoholic solution. The regenerated l-benzylmethylcarbinol had b. p. 108°/21 mm., and $\alpha_{5461}^{23°}$ — 32·18°, whereas the d-alcohol used for the preparation of the sulphonate had $\alpha_{5461}^{23°}$ + 33·02°.

The lower-boiling portions of the distillate were heated with alcoholic sodium hydroxide and from the product any active alcohol present was removed in the usual way with phthalic anhydride. The product obtained was separated by distillation into two fractions: A. b. p. 78—79°/20 mm., B. b. p. 90—95°/20 mm.

A weighed about 1·5 grams and consisted mainly of an unsaturated hydrocarbon. B, when redistilled, had b. p. 93°/19 mm., $n_{5896}^{25°}$ 1·4909, $d_4^{24°}$ 0·9230, and $\alpha_{5461}^{21°}$ — 10·96° in a 50-mm. tube. Its refractive index and density are thus both somewhat higher than those obtained for the ethyl ether of benzylmethylcarbinol by the other methods.

This experiment was repeated using a partly active alcohol ($\alpha_{5461}^{21°}$ — 7·82°), which gave a p-toluenesulphonate having $[\alpha]_{5461}$ — 6·92° in benzene solution. Twenty grams of this ester, dissolved in 120 c.c. of alcohol, were heated under reflux with 14 grams of potassium acetate; 3·8 grams of benzylmethylcarbinyl acetate were isolated, b. p. 107°/14 mm., d_4^{20} 0·9968, n_{5896}^{20} 1·4897, and $\alpha_{5461}^{20°}$ + 2·0°. On hydrolysis it yielded a benzylmethylcarbinol having $\alpha_{5461}^{20°}$ + 7·44°.

Other products of the reaction were a hydrocarbon and the ethyl ether of benzylmethylcarbinol, which were not completely isolated owing to the small bulk of the mixture.

Reaction between Benzylmethylcarbinyl p-Toluenesulphonate and Potassium Acetate when dissolved in Glacial Acetic Acid.—Nineteen grams of the sulphonate ($[\alpha]_{5461}$ — 6·92° in benzene solution), prepared from an alcohol having α_{5461}^{21} —7·82°, were dissolved in 100 c.c. of glacial acetic acid. The mixture was warmed for twenty-four hours on a water-bath and remained quite clear. It was poured into water, the acid neutralised with sodium carbonate, and the solution extracted with ether. The product obtained from the ethereal extract was carefully fractionated. After three distillations, 5·7 grams of benzylmethylcarbinyl acetate were obtained which had $d_4^{2?}$ 0·9961, $n_{5896}^{21·5}$ 1·4896, and $\alpha_{5461}^{2?°}$ + 1·06°. This on hydrolysis gave an alcohol having α_{5461}^{21} + 3·74°, $n_{5896}^{20°}$ 1·5214, and d_4^{20} 0·9879.

Reaction between Benzylmethylcarbinyl p-Toluenesulphonate and Potassium n-Valerate.—Potassium n-valerate was prepared by neutralising n-valeric acid with the theoretical quantity of potassium carbonate dissolved in the minimum of water, and evaporating the mixture to dryness. Forty grams of the residue were dissolved in 182 grams of absolute alcohol and 90 grams of benzene, and the solution dried by distillation until the temperature was 78·3°. Thirty grams of the sulphonate prepared from benzylmethylcarbinol ($\alpha_{5461}^{21°}$ — 24·94°) were added to the alcoholic solution, and the mixture was heated under reflux for six hours. On isolation of the product as described in previous experiments, 9·5 grams of benzylmethylcarbinyl n-valerate were obtained, b. p. 147—148°/19 mm., $d_4^{25°}$ 0·9605, $n_{5896}^{21°}$ 1·4817, and $\alpha_{5461}^{16·5}$ + 9·76°. On hydrolysis, it gave an alcohol having $\alpha_{5461}^{20°}$ + 23·98°.

During this reaction also, the lower fractions obtained were small in bulk and consisted largely of benzylmethylcarbinyl ethyl ether.

Reaction between Sodium Phenoxide and Benzylmethylcarbinyl p-*Toluenesulphonate.*—To a solution of sodium phenoxide in absolute alcohol prepared from 5·6 grams of phenol and 1·35 grams of sodium, 17 grams of benzylmethylcarbinyl p-toluenesulphonate, prepared from a partly active alcohol (α_{5461}^{17} $-$ 6·44°), were added, and the mixture was heated under reflux for four hours. The alcohol was distilled off, the residue poured into a dilute solution of sodium hydroxide, and after extraction with ether, fractional distillation of the product gave two main fractions : (1) an unsaturated substance, about 2 grams, b. p. 68—70°/14 mm. ; (2) benzylmethylcarbinyl phenyl ether, 4 grams, b. p. 156—157°/14 mm., $\alpha_{5461}^{18°}$ $+$ 14·12°, d_4^{20} 1·0288, n_D^{20} 1·5573, and $[R_L]_{5806}^{20°}$ 66·40 (calc. 65·91).

Reaction between Phenyl p-*Toluenesulphonate and the Potassium Derivative of Benzylmethylcarbinol.*—Twelve grams of partly active alcohol ($\alpha_{5461}^{17°}$ $-$ 6·44°) were added to 120 c.c. of dried benzene, in which were suspended 3 grams of finely divided potassium. When all the metal had dissolved, a benzene solution of 20 grams of phenyl p-toluenesulphonate was added. The solution remained clear for some time, then a voluminous precipitate suddenly formed. The mixture, having been heated under reflux for five hours, and sodium hydroxide added, was distilled with steam. The distillate was extracted with benzene, and the residue from the dried benzene extract distilled. Three fractions were obtained : A, b. p. 70—80°/17 mm. (less than 1 gram). B, b. p. 103°/17 mm. (7 grams). C, b. p. 157—160°/17 mm. (1·5 grams).

A appeared to be identical with the hydrocarbon previously obtained. B was benzylmethylcarbinol having $\alpha_{5461}^{18°}$ $-$ 4·36°, whilst C was similar to the phenyl ether obtained in the previous experiment and had $\alpha_{5461}^{18°}$ $+$ 10·20°.

Although the sign of rotation of this ether is definite, the magnitude of the rotation is not above suspicion, since the small amount obtained made efficient purification difficult.

VI.—*Nitration of 3-Chloroacenaphthene.*

By GLADYS FARNELL.

IN the nitration of 3-chloroacenaphthene, described below, a uniform product was not obtained, and it can be shown that the nitro-group has taken up alternative positions. *3-Chloro-4-nitro-acenaphthene*, m. p. 136—138°, was isolated, and its constitution proved. A second product, not entirely uniform and melting at 160—166°, was obtained, and this also appears to be a mononitro-derivative of chloroacenaphthene.

Nitration.—Twenty grams of 3-chloroacenaphthene, m. p. 69°, prepared by Crompton and Walker's method (T., 1912, **101**, 958) and purified by distillation and crystallisation from alcohol, were dissolved in the minimum quantity of glacial acetic acid, and 4·4 c.c. of nitric acid (*d* 1·5) so added, with vigorous shaking, that no appreciable temperature change occurred. The liquid, which changed from yellow to red, deposited crystals, long, pale yellow needles after three hours and, later, spherical clusters. By repeated crystallisation from alcohol, it was possible to isolate from the crude product the two compounds already mentioned, melting at 160—166° and 136—138°, respectively, which are formed in about equal quantity. The final yield of the latter was only 10 per cent. of the theoretical; attempts to improve the yield by varying the conditions of the nitration were not successful [Found : N = 6·07, 6·06; Cl, by the lime method, = 15·23, 15·08, by Rosenmund's method (*Ber.*, 1918, **51**, 578), = 15·30. $C_{12}H_8O_2NCl$ requires N = 6·02; Cl = 15·20 per cent.].

The results indicate that the compound is a mononitrochloro-acenaphthene. A study of its reduction products served to establish its constitution.

Reduction.—The chloronitroacenaphthene was first reduced with sodium hyposulphite by Sachs and Mosebach's method (*Ber.*, 1911, **44**, 2855). The product after purification by crystallisation from hot water was colourless and melted at 145° (Found : Cl, by Rosenmund's method, = 16·89. $C_{12}H_8NCl$ requires Cl = 17·45 per cent.).

Chloroaminoacenaphthene crystallises in fine, colourless needles from water, alcohol, or alcohol–water mixtures. It darkens on heating or on exposure to light. Its solutions are coloured blue by ferric chloride, and, in the presence of acid, give a green precipitate with sodium nitrite. In these points it closely resembles the ordinary aminoacenaphthene, in which, as shown by Graebe (*Annalen*, 1903, **327**, 81), the amino-group is in the position 3

(or 4). This analogous behaviour suggested that the amino-groups in the two compounds are in similar positions, which could only be the case if the nitro-group had originally entered 3-chloro-acenaphthene in the position 4. Were this so, the replacement of the chlorine of the above chloroaminoacenaphthene by hydrogen should yield the familiar 3-aminoacenaphthene.

Such a replacement occurs in the reduction with hydrogen described above, but a simpler method of arriving at the same result was discovered in the direct reduction of the original chloronitroacenaphthene. This compound was reduced with hydrogen in the presence of palladium. It was found that, in addition to the removal of the chlorine, the nitro-group was reduced to an amino-group. When purified, the amino-compound thus obtained resembled 3-aminoacenaphthene perfectly in its appearance and behaviour. It melted at 107°, alone or mixed with this substance, and gave the colour reactions with ferric chloride and sodium nitrite already described. It is therefore the aminoacenaphthene of known constitution, with the amino-group in the position 3 (or 4). The production of this compound by the direct reduction of the chloronitroacenaphthene, melting at 136—138°, in which chlorine is in the position 3, proves that the nitro-group is in the position 4.

On oxidation with chromic acid, it gives the corresponding *chloronitronaphthalic acid*. This was obtained as a yellow powder, and, on crystallisation from glacial acetic acid, it gave pale yellow, shining leaflets of the *anhydride* (Found : N = 4·69. $C_{12}H_4O_5NCl$ requires N = 5·04 per cent.). *Sodium, calcium,* and *barium* salts were prepared, and the calcium salt was analysed (Found : Ca = 11·76, 11·69. $C_{12}H_4O_6NClCa$ requires Ca = 11·99 per cent.).

The compound melting at 160—166°, formed along with the above chloronitroacenaphthene in the nitration of 3-chloroacenaphthene, was not obtained in sufficient quantity in a pure state for its complete examination. It was found to contain 6·04 per cent. of nitrogen, and therefore is probably also a mononitrochloroacenaphthene, or a mixture of such compounds.

This work was suggested to me by Mr. H. Crompton, and I am ndebted to him for guidance in carrying it out.

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VII.—*The Chemistry of the Glutaconic Acids.* Part XIII. *The Isomerism due to Retarded Mobility.*

By JOCELYN FIELD THORPE and ARTHUR SAMUEL WOOD.

EARLY this year, Feist (*Annalen*, 1922, **428**, 25) published a theoretical discussion of the evidence which has accumulated during the past seventeen years regarding the structure of the glutaconic acids and reached the general conclusion that the isomerism of these acids is of the " ordinary " geometrical type and that the adoption of a symmetrical formula for glutaconic acid is unnecessary. He supports his conclusion by some further experimental work embodied in three papers (with Breuer, *ibid.*, 59, 68; and with Breuer and Lubricht, *ibid.*, 40), in two of which he deals with the products formed by the decomposition of the ozonides of certain acids of the series, and, in the third, with the question of the existence of the three isomerides of β-phenyl-α-methylglutaconic acid isolated by us (T., 1913, **103**, 1574).

Feist gives an excellent summary of the experimental facts which have led to the conclusion that the formulæ of glutaconic acid, and those of its derivatives which contain a mobile hydrogen atom, must differ from those of the ordinary unsaturated dicarboxylic acids in some fundamental manner, but, unfortunately, he does not criticise these facts or their theoretical bearing in detail, and therefore it is difficult to follow his general reasoning. Nevertheless, it would seem that our views and his are not, in reality, very different, because when he says that " the absence of a second form of glutaconic acid is readily explicable on the assumption that the double bond changes position," he can only mean that the absence of isomerism is due to symmetry, because it is obvious that any movement of the double bond in glutaconic acid will produce—as does the movement of the double bonds in either of the Kekulé benzene individuals—a substance having an identical space formula. It is true that he guards himself by the alternative " oder ausschliesslich die stabilere *trans*-modification bilden wird," but, of course, this cannot be the case, because the only known form of glutaconic acid is a *cis*-form, that is, it readily passes into the anhydride, a behaviour which is quite different from that of the known *trans*-forms of the series, such as *trans*-αα-dimethylglutaconic acid or *trans*-ααβ-trimethylglutaconic acid, which do not form anhydrides, or, for the matter of that, of the *trans*-modification of β-phenyl-α-methylglutaconic acid, which he himself mentions in his paper.

In his ozone experiments, Feist prepares the ozonides of the two

forms of αβ-dimethylglutaconic acid and of his two forms of β-phenyl-α-methylglutaconic acid and studies the products obtained from them on degradation. If, however, such evidence were accepted as proof of structure, the formula of benzene would have been settled when Harries carried out his classical researches on the formation and degradation of its ozonide. Still, the experiments described by Feist are instructive, because they show that the ozonides from both the " *cis* " and " *trans* " forms of ethyl β-phenyl-α-methylglutaconate yield the same four products and that two pairs of these are those which would normally have been derived from two esters having the formulæ $CO_2Et·CH_2·CPh:CMe·CO_2Et$ and $CO_2Et·CH:CPh·CHMe·CO_2Et$, respectively. In other words, the behaviour towards ozone is exactly that which one would expect if the esters had reacted in the " normal " form. Finally, Feist has succeeded in isolating only two forms of β-phenyl-α-methylglutaconic acid. One of these is the *trans*-labile modification (m. p. 155°) described by us (*loc. cit.*). The other melts at 151° and is evidently a *cis*-acid, because it is readily converted into an anhydride (m. p. 94°). The two other acids of this formula prepared by us were the " normal " acid (m. p. 120°) and the *cis*-labile acid (m. p. 108°). Feist considers that these two acids are impure specimens of his acid (m. p. 151°), and attempts to prove his point by determining the melting points of varying mixtures of the *trans*-labile acid (m. p. 155°) and his *cis*-acid (m. p. 151°). As our acids were made by the hydration of the pure anhydride, it is not possible for them to have contained any of the *trans*-modification. Moreover, our acids were pure compounds and the repeated recrystallisation of specimens which remained in our possession has failed to alter the melting points given above. The explanation of the discrepancy in our results and those of Feist without doubt rests on the fact that the anhydride (hydroxy-anhydride) prepared by Feist from his acid melting at 151° is a different substance from that prepared by us from the acids melting at 120° and 108°, respectively. The two anhydrides melt at much the same temperature, but they react very differently on hydration, and although we have not succeeded in isolating the pure anhydride prepared by Feist, we have been able to show that our anhydride is, at any rate partly, converted into Feist's anhydride when it is distilled under diminished pressure. This follows, because a specimen of our anhydride which before distillation gave, on hydration, the acids melting at 120° and 108° as sole products, yielded, after distillation, a mixture of acids from which we were able to isolate a small quantity of Feist's *cis*-acid melting at 151°.

It is evident, therefore, that in a glutaconic system such as that

which is contained in the molecule of β-phenyl-α-methylglutaconic acid, the mobility of the hydrogen atom is so far decreased as to render possible the isolation of two forms of the hydroxy-anhydride which can be represented by the formulæ I and II.

$$
\begin{array}{ccc}
\mathrm{CMe\text{-}CO} & \mathrm{CMe{=}C(OH)} & \mathrm{CHMe\cdot CO_2H} \\
\mathrm{CPh}\quad\diagdown\mathrm{O} & \mathrm{CPh}\quad\diagdown\mathrm{O} & \mathrm{CPh} \\
\mathrm{CH{=}C(OH)} & \mathrm{CH{-}CO} & \mathrm{CH\cdot CO_2H} \\
(\text{I.}) \ast & (\text{II.}) & (\text{III.})
\end{array}
$$
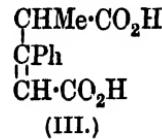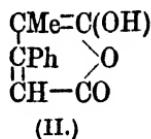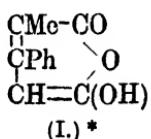
M. p. 94° (T. and W.).   M. p. 93—94° (F.).   cis-acid, m. p. 151° (F.).

The hydroxy-anhydride (II) gives, on hydration, Feist's acid (III), and the hydroxy-anhydride (I) a mixture of the " normal " acid (IV) and the cis-labile acid (V); the trans-acid being represented by (VI).

$$
\begin{array}{ccc}
\cdot\mathrm{CMe\cdot CO_2H} & \mathrm{CMe\cdot CO_2H} & \mathrm{CO_2H\cdot CMe} \\
\mathrm{CHPh} & \mathrm{CPh} & \mathrm{CPh} \\
\cdot\mathrm{CH\cdot CO_2H} & \mathrm{CH_2\cdot CO_2H} & \mathrm{CH_2\cdot CO_2H} \\
(\text{IV.}) \ast & (\text{V.}) \ast & (\text{VI.}) \ast
\end{array}
$$
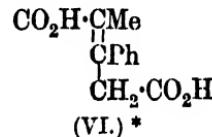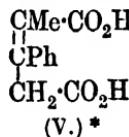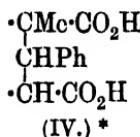
M. p. 120° (T. and W.).   M. p. 108° (T. and W.).   M. p. 155° (T. and W., F.).

Two other compounds of this formula should also be capable of isolation, namely, the trans-acid (VII) corresponding with Feist's cis-acid (III), and the " normal " anhydride (VIII),

$$
\begin{array}{ccc}
(\text{VII.}) & \begin{array}{c}\mathrm{CHMe\cdot CO_2H} \\ \mathrm{CPh} \\ \mathrm{CO_2H\cdot CH}\end{array} & \begin{array}{c}\cdot\mathrm{CMe\text{-}CO} \\ \mathrm{HCPh}\quad\diagdown\mathrm{O} \quad (\text{VIII.}) \\ \cdot\mathrm{CH{-}CO}\end{array}
\end{array}
$$
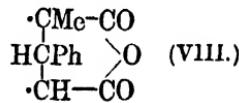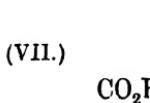
but we have not as yet been able to isolate these substances.

From these experiments it would appear, therefore, that a glutaconic acid, in which the presence of groups in the three-carbon system so far retards the movement of the tautomeric hydrogen atom as to enable it to remain within either the three-carbon system or one or other of the systems C·C·O, can be isolated in five forms—two trans-, two cis-, and one " normal."

THE IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
S. KENSINGTON.   [Received, December 1st, 1922.]

* The structures of the compounds marked * are, we consider, fixed by the fact that the three acids IV, V, and VI give isobutenylbenzene, CHMe:CPh·CH₃, when they are boiled with dilute mineral acid (compare Thorpe and Wood, loc. cit., p. 1572).

VIII.—*The Higher Oxide of Cobalt.*

By OWEN RHYS HOWELL.

THE precipitation of a higher oxide of cobalt from solution by means of alkali and an oxidising agent has received considerable attention (Bayley, *Chem. News*, 1879, **39**, 81; Carnot, *Compt. rend.*, 1889, **108**, 610; Schröder, *Chem. Zentr.*, 1890, i, 931; Vortmann, *Ber.*, 1891, **24**, 2744; McLeod, *Rep. Brit. Assoc.*, 1892, 669; Mawrow, *Z. anorg. Chem.*, 1900, **24**, 263; Hüttner, *ibid.*, 1901, **27**, 81; Metzl, *ibid.*, 1914, **86**, 358), but the nature of the oxide does not appear to have been satisfactorily established. An attempt was therefore made to throw light on the subject by a quantitative examination of the precipitates formed by the action of alkaline hypochlorites on cobalt sulphate. In one series of experiments, the cobalt salt was precipitated with sodium hydroxide and sodium hypochlorite; in a second series, lime and bleaching powder were used.

EXPERIMENTAL.

Materials.—The cobalt sulphate was free from nickel and contained only a trace of iron. The sodium hypochlorite was made by passing washed chlorine into aqueous sodium hydroxide below 15° until chlorination was almost complete, a little free alkali being left to retard decomposition of the hypochlorite. The calcium hypochlorite was prepared by extracting bleaching powder with water.

Method of Investigation.—A solution containing 15 grams of cobalt sulphate in 100 c.c. of water was precipitated with the requisite amount of alkali and hypochlorite dissolved in 500 c.c. of water, after determining accurately the concentration of the hypochlorite (by liberation of iodine) and of the alkali (by adding hydrogen peroxide to remove the hypochlorite and then titrating, due allowance being made for the acidity of the hydrogen peroxide). The mixture was stirred for two hours, during which any excess of hypochlorite was decomposed by the catalytic action of the oxide. The precipitate was allowed to settle over-night, filtered on a Buchner funnel, washed, collected in a porcelain dish, and weighed. For analysis, samples of about 2 grams were weighed in small tubes, and dropped into a solution of potassium iodide acidified with hydrochloric acid; the liberated iodine was titrated and the available oxygen calculated.

In later experiments, the suspended precipitate was titrated immediately after the completion of the decomposition of the

hypochlorite without waiting for it to settle. In this way it was established that the oxide, once formed, is quite stable, since the same value was found for the available oxygen immediately after precipitation and after the precipitate had been kept for some weeks.

Action of Hypochlorite Alone.—The following results were obtained with sodium hypochlorite free from alkali :

<div align="center">TABLE I.</div>

Equivalents of NaOCl.	Equivalents of available oxygen in the precipitate.	
	Per equivalent of Co taken.	Per equivalent of Co precipitated.
0·776	0·471	1·050
1·400	0·700	1·045
1·960	0·786	1·050
2·494	0·834	1·056
3·576	0·885	1·048
4·988	0·934	1·053

The amount of available oxygen was estimated as described above and the amount of cobalt in the precipitate was also estimated in each case by taking an aliquot part of the suspension of the oxide, filtering, washing, and reducing to metal in a stream of hydrogen. The composition of the precipitate is seen to be independent of the amount of hypochlorite used, the proportion of available oxygen being constant at 1·05 equivalents. The direct action of the hypochlorite is therefore to yield the sesquioxide, which would contain 1 equivalent of available oxygen.

The results are shown graphically in Fig. 1, where the amount of available oxygen found in the precipitate is plotted against the total amount taken. The slope of the curve indicates that the reaction proceeds initially according to the equation

$$2CoSO_4 + 3NaOCl + H_2O = Co_2O_3 + O + 2NaHSO_4 + NaCl + Cl_2,$$

the course of which is represented by the tangent ($NaOCl : Co_2O_3 = 3 : 1$) in Fig. 1 (A); but as the amount of hypochlorite is increased there is probably an increased tendency to produce neutral sodium sulphate, as shown in the equation

$$2CoSO_4 + 4NaOCl = Co_2O_3 + O + 2Na_2SO_4 + 2Cl_2.$$
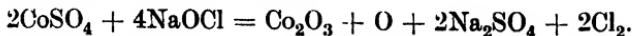
Since the composition of the precipitate is constant, its content of available oxygen is a measure of the amount of cobalt precipitated; the ordinates denoting this quantity fall away rapidly from the tangent, showing that a very large excess of hypochlorite would be necessary to secure complete precipitation of the cobalt. This is attributed to the fact that the particles of sesquioxide appear to be coated with a higher oxide which catalytically decomposes

the hypochlorite, an action that is specially rapid in these alkali-free solutions.

Action of Hypochlorite in Presence of Alkali.—A constant excess of alkali was used with varying amounts of hypochlorite. The results obtained with the sodium compounds are given in Table II and those with the calcium compounds in Table III. The values are plotted in Fig. 1 (B).

FIG. 1.
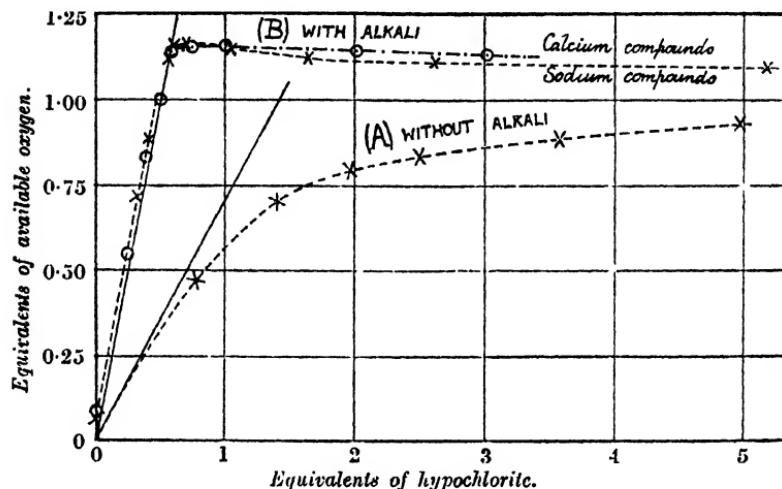
TABLE II.

NaOH.	Na$_2$CO$_3$.	Total alkali.	NaOCl.	Available oxygen in the precipitate.
1·469	0·044	1·513	Nil	0·060
1·400	0·022	1·422	0·320	0·712
1·400	0·022	1·422	0·405	0·886
1·421	0·011	1·432	0·562	1·119
1·421	0·022	1·443	0·601	1·155
1·410	0·011	1·421	0·703	1·162
1·341	0·069	1·410	1·051	1·149
1·421	0·022	1·443	1·640	1·121
1·390	0·045	1·435	2·629	1·106
1·406	0·022	1·428	5·192	1·095

TABLE III.

Ca(OH)$_2$.	Ca(OCl)$_2$.	Available oxygen in the precipitate.	Ca(OH)$_2$.	Ca(OCl)$_2$.	Available oxygen in the precipitate.
1·192	Nil	0·084	1·181	0·745	1·151
1·192	0·248	0·550	1·192	1·007	1·142
1·192	0·396	0·829	1·192	2·002	1·140
1·187	0·507	1·000	1·215	3·026	1·130
1·204	0·596	1·142			

In every case the quantities are given in equivalents per equivalent of cobalt, the equivalent of a hypochlorite being taken as the quantity which contains 8 grams of available oxygen. Since, in presence of an excess of alkali, precipitation is always complete, the available oxygen calculated on the cobalt taken is the same as on the cobalt precipitated.

It is seen that, owing to atmospheric oxidation of the hydroxide, the precipitate contains more oxygen than that supplied by the hypochlorite so long as the quantity of the latter is less than the quantity (half an equivalent) that is required to oxidise all the hydroxide to sesquioxide. If more than this quantity is added, oxidation again proceeds beyond the stage of sesquioxide, and the peroxide so formed catalytically decomposes the hypochlorite.

Equivalents of alkali.
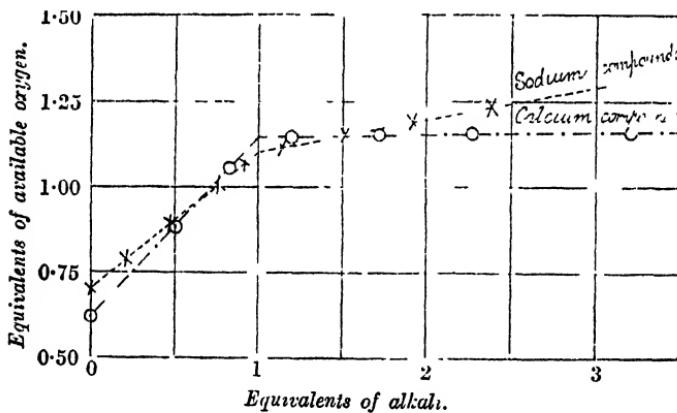
Since, however, the peroxide appears to be stabilised by the excess of alkali (see p. 69), the action of the hypochlorite proceeds further than when hypochlorite is used alone, the extent depending on the excess of alkali. When still more hypochlorite is used, the available oxygen in the precipitate falls off towards the slightly lower value given by hypochlorite alone.

Action of Alkali.—A constant amount of hypochlorite was used with variable amounts of alkali. The results with the sodium compounds are given in Table IV and those with the calcium compounds in Table V. The values are plotted in Fig. 2. The two curves are not directly comparable because the precipitating solutions were not of the same composition in the two cases.

Both curves exhibit a break at one equivalent of alkali. Up to this point the precipitation of the cobalt is incomplete, since in the absence of alkali a very large excess of hypochlorite is required

TABLE IV.

NaOH.	Na$_2$CO$_3$.	Total alkali.	NaOCl.	Available oxygen in the precipitate calculated on	
				(i) cobalt taken.	(ii) cobalt precipitated.
Nil	Nil	Nil	1·400	0·700	1·050
0·190	0·032	0·222	1·393	0·786	1·059
0·462	0·020	0·482	1·393	0·895	1·072
0·740	0·018	0·758	1·400	1·002	1·075
0·908	0·018	0·926	1·416	1·072	1·089
1·104	0·011	1·115	1·393		1·106
1·502	0·018	1·520	1·393		1·150
1·910	0·011	1·921	1 400		1·184
2·342	0·042	2·384	1·400		1·226
2·910	0·023	2·933	1·400		1·280

TABLE V.

Ca(OH)$_2$.	Ca(OCl)$_2$.	Available oxygen calculated on	
		(i) cobalt taken.	(ii) cobalt precipitated.
0·011	1·143	0·619	1·052
0·512	1·153	0·881	1·097
0·821	1·147	1·055	1·125
1·200	1·153		1·140
1·721	1·153		1·150
2·278	1·153		1·152
3·206	1·143		1·156

to throw down all the cobalt, whereas the precipitation of the cobalt by alkali is quantitative. The figures in the last column show that the precipitate is in every case a slightly peroxidised sesquioxide; the proportion of available oxygen which it contains is, however, not constant, but increases with the amount of alkali that is used. In the case of sodium hydroxide, the increase continues when the alkali is in excess of one equivalent and is even more rapid than when smaller quantities of alkali are being used to precipitate the cobalt. In the case of lime, this secondary increase in presence of an excess of alkali does not take place, since the active mass of the calcium hydroxide is limited by its sparing solubility.

The lowest figures in the last column of Tables IV and V are those given by hypochlorite alone, even when present in large excess. Some additional factor must therefore be introduced to account for the higher degree of oxidation which results from the use of alkali. For this reason, it is suggested (i) that cobalt hydroxide is more readily peroxidised than cobalt sulphate and (ii) that the peroxide thus formed is perhaps hydroxylated, for example, OH·Co·O·OH, and in this form is more stable than cobalt peroxide precipitated directly from solution by sodium hypochlorite.

Action of Sodium Carbonate.*—A number of experiments have been made in which the cobalt solution was precipitated with a mixture of sodium carbonate and sodium hypochlorite. Under these conditions, an almost black, gelatinous precipitate is obtained, and a green solution, which deposits the black substance slowly, but more rapidly on dialysis. The green solution appears to be colloidal and gives the Tyndall cone. The precipitate contains the carbonate radicle in addition to " available " oxygen and appears to be a peroxidised carbonate. This action will be made the subject of further investigation.

Influence of Temperature.—In this series of experiments, the composition of the reacting solutions was the same in each case. Both solutions were warmed to the requisite temperature before mixing and kept at this temperature while stirred for half an hour.

(*a*) Precipitating solution, NaOH 1·35 equivs.   NaOCl 1·35 equivs.

Temp. of precipitation ...	15°	30°	60°	80°	80° †
Available oxygen	1·156	1·175	1·180	1·179	1·181

(*b*) Precipitating solution, $Ca(OH)_2$ 1·24 equivs. $Ca(OCl)_2$ 1·40 equivs.

Temp. of precipitation	15°	30°	42°	60°	80°	70° †
Available oxygen	1·150	1·157	1·161	1·166	1·167	1·157

† After boiling for four hours.

It is evident that the temperature of precipitation has practically no influence on the composition of the precipitate formed. Moreover, the substance is a very stable one, for even after boiling for four hours there was no decrease in the content of oxygen.

Influence of Concentration.—In this series of experiments all conditions were constant except the concentrations of the reacting solutions. In B, the concentration was the same as in all previous experiments; in A, it was half, and in C double, this value.

(*a*) Precipitating solution, NaOH 1·35 equivs.   NaOCl 1·35 equivs.

	A.	B.	C.
Concentration	half	unity	double
Available oxygen	1·150	1·150	1·156

(*b*) Precipitating solution, $Ca(OH)_2$ 1·68 equivs. $Ca(OCl)_2$ 1·46 equivs.

	A.	B.	C.
Concentration	half	unity	double
Available oxygen	1·147	1·150	1·155

* Compare Durrant (P., 1896, **12**, 244) and McConnell and Hanes (T., 1897, **71**, 589), who have examined the precipitation of cobalt solutions by bicarbonates and hypochlorites.

It is evident from these figures that the concentration of the reactants has practically no influence on the composition of the precipitate.

Summary.

1. Hypochlorites free from alkali immediately precipitate from aqueous solutions of cobalt sulphate a slightly peroxidised cobalt sesquioxide of constant composition containing about 1·05 equivalents of available oxygen; but since the peroxide catalytically decomposes the hypochlorite, the precipitation is far from quantitative.

2. When less than half an equivalent of hypochlorite is used with an excess of alkali, more available oxygen is found in the precipitate than was used in the hypochlorite; this is attributed to atmospheric oxidation of the precipitated hydroxide.

3. A higher degree of oxidation is reached with hypochlorite and alkali than with hypochlorite alone. This is attributed to the formation of a hydroxylated peroxide, by direct oxidation of cobaltous hydroxide.

4. The temperature has no important influence on the composition of the precipitate. The oxide is very stable, since it can be kept indefinitely and prolonged boiling causes no loss of available oxygen.

5. The concentration of the reacting solutions likewise has practically no influence on the composition of the precipitate.

IX.—The Relation between the Crystal Structure and the Constitution of Carbon Compounds. Part I. Compounds of the Type CX_4.

By Isabel Ellie Knaggs.

Considering the large number of organic compounds which have been examined crystallographically, it is remarkable that no kind of comprehensive generalisation connecting their crystalline form with their molecular structure appears to have been reached. Yet

it is abundantly clear that a connexion between the two must exist, and no doubt the difficulty which workers have had in interpreting their results is to be traced to the complexity of the relationship.

The extensive investigations which have been carried out in the X-ray analysis of crystals since von Laue's discovery in 1912 of the diffraction of X-rays by crystals have already gone far to solve the problem as regards inorganic compounds. But in organic compounds the structures are essentially more complex and present difficulties in the way of X-ray analysis which it will not be easy to surmount. In the case of aromatic carbon compounds, recent work of Sir William Bragg (*Proc. Physical Soc.*, 1921, **34**, 1) on the X-ray analysis of naphthalene and anthracene has afforded striking evidence of the persistence of the benzene ring in one of its forms and therefore perhaps also of the chemical molecule in the crystalline state. If this should be generally applicable to aromatic compounds, the problem in their case would be considerably simplified.

In the case of the aliphatic compounds, however, no such evidence is yet to hand, and at the present stage of the problem it would appear that it is only as the result of the examination of the crystalline form of the simplest molecular types and the observation of regularities which they present that any progress can be expected. Therefore at the outset of the investigation, of which the present communication constitutes a preliminary part, it is proposed to examine those aliphatic compounds which are simplest in molecular structure.

Before these experiments were commenced or the literature searched, the author held, as a working hypothesis, that the most symmetrical molecular structures should give rise to the most symmetrical crystallographic forms, although the converse would not necessarily be true. Thus, the most symmetrical of all types, namely, the type CX_4, in which X is an element or symmetrical group such as CH_3, and which itself possesses cubic symmetry (although not the highest symmetry possible in that system) should give rise to crystals of the cubic system; whilst compounds of this type in which X is a less symmetrical group should give rise to tetragonal crystals. Considered as an expression of what is undoubtedly a strong general tendency, this hypothesis * is fully borne

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* This rule has already been of service in providing evidence of constitution. The synthesis of methanetetra-acetic acid has recently been described by Ingold and Nickolls (T., 1922, **121**, 1645) and its crystallographic properties are given on p. 78. When this acid was first prepared there was doubt as to its constitution, which might have been that corresponding with any one of the formulæ $C(CH_2 \cdot CO_2H)_4$, $(CO_2H \cdot CH_2)_2CH \cdot CH(CO_2H) \cdot CH_2 \cdot CO_2H$, and $CO_2H \cdot CH_2 \cdot CH_2 \cdot C(CO_2H)(CH_2 \cdot CO_2H)_2$. The crystallographic evidence pointed

out by the evidence brought forward in this paper and is in agreement with the conclusions drawn by Wahl (*Proc. Roy. Soc.*, 1914, [*A*], **90**, 1) as a result of the optical investigations of a number of simple carbon compounds. The modifications necessary in its detailed application will be discussed hereunder.

The first case which has to be considered is that in which X is a single univalent element. There are four examples on record: Wahl has examined the crystalline form of methane (*ibid.*, 1912, [*A*], **87**, 377) and of carbon tetrachloride (*ibid.*, 1913, [*A*], **89**, 330), Wahl (*loc. cit.*) and Zirngiebl (Groth, "Chem. Kryst." I, 330) carbon tetrabromide, and Gustavson (*op. cit.*, p. 229; *Annalen*, 1874, **172**, 173) carbon tetraiodide. Methane itself crystallises below −185·8° in the cubic system. Carbon tetrachloride at −22° crystallises in grains, which are isotropic and therefore belong to the cubic system, but at −47° a transition into a doubly refracting mass takes place.

Carbon tetrabromide crystallises in the cubic system above 46°, there being a transition at that temperature into a monoclinic variety, which, however, has a marked cubic habit, the crystals very closely approaching regular octahedra. Carbon tetraiodide crystallises in octahedra, which are isotropic and therefore cubic in symmetry; no accurate measurements have been made owing to the unstable character of the compound.

There does not appear to be an example of a substance CX_4 in which X is a group of two atoms, but an instance of one in which X is a group of three atoms is provided by tetranitromethane, which has been examined by Wahl (*Proc. Roy. Soc.*, 1913, [*A*], **89**, 333). This substance crystallises in the cubic system, although at low temperatures there is a transition into a modification which shows very weak double refraction and probably belongs to a uniaxial system. Of compounds in which X is a group of four atoms, one of which must necessarily be carbon or some other quadrivalent element, an example is afforded by tetramethylmethane, which Wahl (*ibid.*, 1913, [*A*], **88**, 359) found to be cubic, with a low-temperature, doubly refracting modification, which is probably tetragonal.

In all these cases, in agreement with the original hypothesis, the crystalline form stable at the higher temperature is cubic. The lower-temperature modification with a lower degree of symmetry shown by four of these compounds may reasonably be supposed to

plainly to a formula of the type CX_4. The first formula was therefore accepted by the investigators concerned as a satisfactory basis for further work and was fully confirmed several months later by purely chemical methods (*loc. cit.*).

be due to a closer packing of the molecular units at lower temperatures.*

The symmetry of a molecule of the type CX_4, in which X is a single atom, is that of a regular tetrahedron, that is, of Evans's CBu (hexakis tetrahedral) class of the cubic system, possessing therefore six diagonal planes of symmetry, the four trigonal symmetry axes of the cubic system, and three digonal axes of ordinary symmetry, which are also tetragonal " contra-directional " (Evans, *Min. Mag.*, 1910, 398) axes or Hilton's (*ibid.*, 1906, 261) axes of the second sort. It might be expected therefore that compounds of this type would crystallise with cubic symmetry, as has actually been found.

Since each of the bonds from the central carbon atom represents one of the four axes of trigonal symmetry essential to all classes of

FIG. 1.

the cubic system, compounds of the type CX_4, in which X is a group of such a nature as not to destroy the trigonal symmetry about these bonds, should yield cubic crystals. The compound tetramethylmethane, $C(CH_3)_4$, is one of these, three hydrogen atoms being arranged symmetrically about a carbon atom at each corner of the tetrahedron (Fig. 1). It is consistent therefore to find this compound crystallising in the cubic system.

In the compound tetranitromethane, $C(NO_2)_4$, the configuration of the nitro-group is uncertain beyond that the nitrogen atom is directly attached to the carbon atom. Of the possible configurations, the linear arrangement, ·N:O:O, is the only one which would allow of the persistence of the four trigonal axes and so lead to the expectation of cubic crystals, as actually found.

Turning now to more complex cases, pentacrythritol, $C(CH_2 \cdot OH)_4$, has been examined by Martin (*Neues Jahrb. Min.*, 1891, Beil. Bd. 7, 18) and found to be tetragonal and to crystallise in the ditetragonal-pyramidal class, that is, the IV Bu class of Evans (*Min. Mag.*, 1907, 360) and therefore to possess a uniterminal axis. The author examined this compound at Cambridge in 1918, and, after repeated

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* An analogy with this behaviour is to be found in that of the minerals andalusite and kyanite, both of which have the chemical composition Al_2SiO_5. Andalusite possesses orthorhombic symmetry, and kyanite only triclinic symmetry. The density of kyanite (3·62) is higher than that of andalusite (3·18), which would indicate closer packing in the less symmetrical variety.
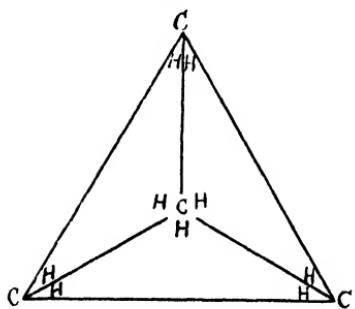
experiments, was unable to find the existence of a uniterminal axis or to assign other than the symmetry of Evans's IV Bc (holohedral) class to the crystals.

Pentaerythritol tetrabromide was found by Jaeger (*Z. Kryst. Min.*, 1908, **45**, 543) to belong to Evans's II Uc class (holohedral) of the monoclinic system. He regards the symmetry as pseudo-cubic, since by a suitable transformation of face symbols an axial ratio of nearly 1 : 1 : 1 and an axial angle of nearly 90° may be obtained.

Pentaerythritol tetranitrate, pentaerythritol tetra-acetate, and methanetetra-acetic acid all crystallise with tetragonal symmetry and with the exception of pentaerythritol tetra-acetate, in which the class is uncertain, in Evans's IV Bc (holohedral) class. They are described in the experimental part of this paper.

Tetraethyl orthocarbonate,

$$C(O \cdot CH_2 \cdot CH_3)_4,$$

FIG. 2.
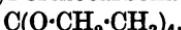
according to Wahl crystallises in the tetragonal system and is pseudo-cubic.

Tetraphenylmethane has been examined by Wahl (*Proc. Roy. Soc.*, 1913, [*A*], **89**, 338), who describes the crystals as needles which optically appear to be orthorhombic.

Of these seven compounds in which X is a complex group, five crystallise in the tetragonal system. Of the remaining two, tetraphenylmethane, crystallising in the orthorhombic system, is perhaps a special case, in which the four phenyl groups have the predominant influence. Pentaerythritol tetrabromide, however, does appear to be an exception to the general rule, though it might be contended that it has a tendency towards a more symmetrical structure as shown by its pseudo-cubic nature.

In molecules of the type CX_4, in which the X groups are of the type CY_2Z, it can easily be seen that the trigonal axes can no longer remain, for there can be no three-fold grouping about the corners of the tetrahedron. The symmetry is reduced to that of Evans's IV Bk (scalenohedral) class of the tetragonal system,* as shown in Fig. 2, which represents the appearance of such a molecule projected on the basal plane.

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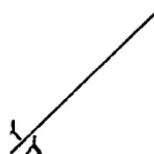
* E. von Fedoroff (*Z. Kryst. Min.*, 1913, **52**, 22) explained the lack of cubic symmetry in crystals of compounds such as pentaerythritol, as due to the carbon atom having a form which is only an approximation to a regular tetrahedron. In the same paper he put forward the view that the " crystal molecule " is composed of several chemical molecules.

By the combination of four such molecular cells in the manner shown in Fig. 3, the symmetry is raised to that of Evans's IV Bu (ditetragonal-pyramidal) class of the tetragonal system, which possesses a uniterminal tetragonal axis and in which, therefore, crystals are unlike at the two ends of that axis.

By a further combination of two such complex cells, one inverted with respect to the other, holohedral tetragonal symmetry, that is, the symmetry of Evans's IV Bc class, may be reached. Such combinations of cells may be regarded as analogous to the ultra-microscopic twinning, considered to be the cause of the assumption of higher symmetry in certain minerals.

From these considerations it might reasonably be expected that compounds of the type $C(CY_2Z)_4$ * would crystallise in any of the classes IV Bk, IV Bu, IV Bc of the tetragonal system. As already stated above, with the exception of pentaerythritol tetrabromide, the remaining five compounds of this type known all crystallise in the tetragonal system and in the case of three of them in the IV Bc (holohedral) class. In the case of two of them, namely, pentaerythritol tetra-acetate and tetraethyl ortho-carbonate, the class has not certainly been determined. That tetraethyl orthocarbon-ate should be included with the compounds of the type $C(CY_2Z)_4$ needs perhaps a little explanation. From its structural formula, co-linear oxygen linkings being assumed, it is evident that the groups at the corners of the tetrahedron are of the type CY_2Z. The linking of each of these groups to the central carbon atom by way of an oxygen atom does not affect the symmetry of the molecule.

Pentaerythritol constitutes a particularly interesting example, since apparently it may assume either the symmetry of the IV Bu (ditetragonal-pyramidal) class as observed by Martin (*loc. cit.*) or that of the IV Bc (holohedral) class as observed by the author.

FIG. 3.

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* It will be seen that in the compounds here discussed Y is hydrogen and, with one exception (in which it is bromine), Z is a complex group, but one which can be so symmetrically arranged as to be equivalent to a single atom as far as the symmetry of a molecule of this type is concerned. The latter will always be the case, provided that Z has a plane of symmetry.
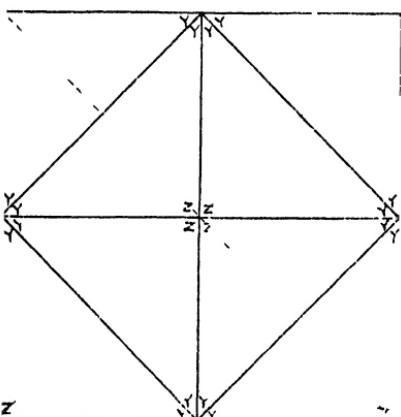
As far as the compounds discussed in this paper are concerned, there is strong evidence that their crystallographic symmetry is an expression of their molecular structure, since from the consideration of their molecular configurations (where these are known) the observed crystallographic symmetry may be deduced. Should this be found by further research to be the case for a large number of organic compounds, it would become legitimate to employ crystallographic evidence in determining stereochemical configurations in cases where these have not yet been determined by chemical methods.

Other compounds of the type CX_4 are in course of preparation for this investigation, and it is proposed also to examine compounds of the type CXY_3 and CX_2Y_2.

EXPERIMENTAL.

Pentaerythritol Tetranitrate, $C(CH_2 \cdot O \cdot NO_2)_4$.

This compound was submitted to me for examination by Sir William Pope and measured by myself at Cambridge in 1918, when working under Dr. Hutchinson's direction.

Crystal system : tetragonal. Class : holohedral. Axial ratio : $a : c = 1 : 0.506$. Forms observed : $A = \{100\}$; $p = \{111\}$.

Angle measured :

	No. of measurements.	Limits.	Mean obs.	Calc.
$Ap - (100) : (111)$	16	65° 37'—65° 46'	65° 42'	65° 42'
$pp - (111) : (\bar{1}11)$	11	48 32 —48 40	48 36	*

Cleavage : {100}, imperfect.

Habit : square, second-order prism terminated by pyramids (Fig. 4). The crystals are colourless and transparent and of a fair size and quality.

Optical characters : refractive indices, as determined by immersion in oils, $\omega = 1.554$, $\varepsilon = 1.553$.

Density : determined by suspension in liquid, $d_4^{20°} = 1.773$ (corr.).

Pentaerythritol Tetra-acetate, $C(CH_2 \cdot O \cdot CO \cdot CH_3)_4$.

Crystal system : tetragonal. Class : uncertain. Axial ratio : $a : c = 1 : 0.324$. Forms observed : $A = \{100\}$, $p = \{111\}$.

Cleavage : perfect basal.

Habit : long, narrow, second-order prisms terminated by blunt or sharp pyramids (Fig. 5). The crystals are colourless and transparent, but extremely small and badly developed. The pyramid faces, when distinguishable, are very minute and the only angular measurement obtainable has been from a face of the blunt

pyramid $p = \{111\}$ on to the prism $A = \{100\}$, this angle being 72° 53′.

Optical characters : refractive indices, as determined by immersion in oils, $\varepsilon = 1\cdot483$, $\omega = 1\cdot433$.

Density : determined by suspension in liquid, $d_4^{18} = 1\cdot213$ (corr.).
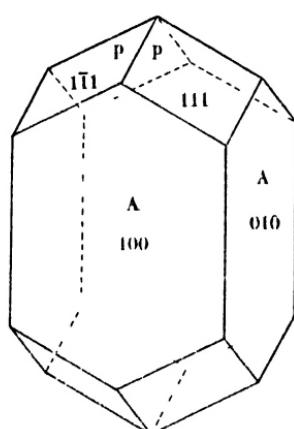
FIG. 4.   FIG. 5.
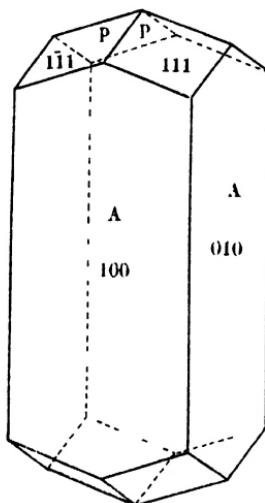
Methanetetra-acetic Acid, $C(CH_2 \cdot CO_2H)_4$.

Crystal system : tetragonal. Class : holohedral. Axial ratio : $a : c = 1 : 0\cdot560$. Forms observed : $m = \{110\}$, $p = \{111\}$.

Angle measured :

	No. of measurements.	Limits.				Mean obs.		Calc.	
$pp = (111):(\bar{1}\bar{1}1)$	9	76°	$23\frac{1}{2}′$—76°	$59\frac{1}{2}′$		76°	45′	76°	47′
$pp = (\bar{1}11):(\bar{1}\bar{1}\bar{1})$	9	102	59	103	$34\frac{1}{2}$	103	11	103	13
$pm = (111):(110)$	12	51	$20\frac{1}{2}$	51	49	51	$33\frac{1}{2}$	51	$36\frac{1}{2}$
$pp = (111):(1\bar{1}1)$	19	51	51	52	18	52	6		*
$pp = (1\bar{1}1):(\bar{1}\bar{1}\bar{1})$	13	127	$45\frac{1}{2}$	128	5	127	$54\frac{1}{2}$	127	54

Cleavage : none observed.

Habit : pyramidal, with short, first-order prisms (Fig. 6). The crystals are extremely small but moderately well developed and are clear and colourless.

Optical characters : refractive indices, as determined by immersion in oils, $\epsilon = 1\cdot518$, $\omega = 1\cdot487$.

Density : determined by suspension in liquid (carbon tetrachloride and light petroleum), $d_4^{23} = 1\cdot460$ (corr.).